Photooxidation Chemistry on TiO_2 Surfaces – Seeing Electrons, Holes and Surface Reaction Processes

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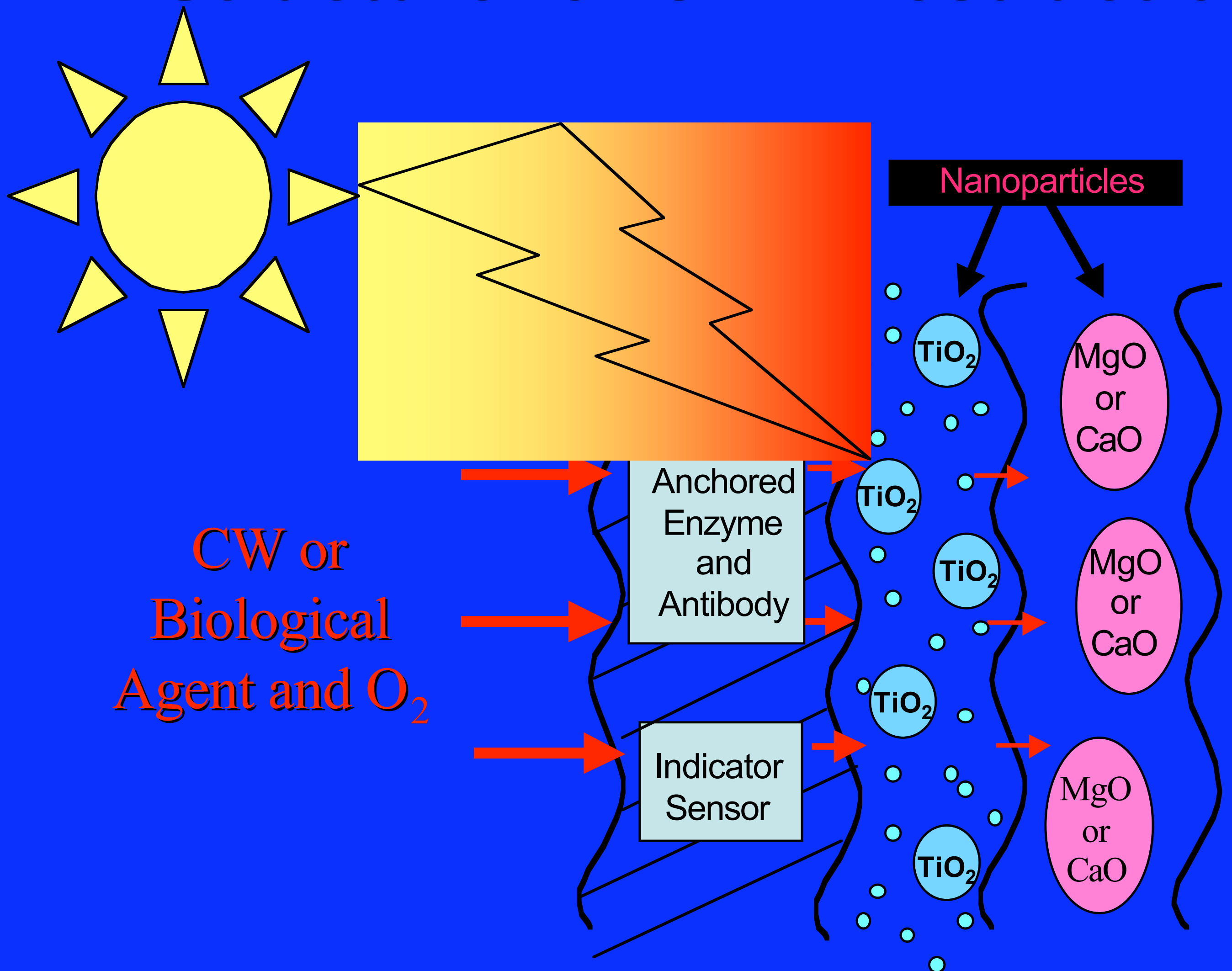
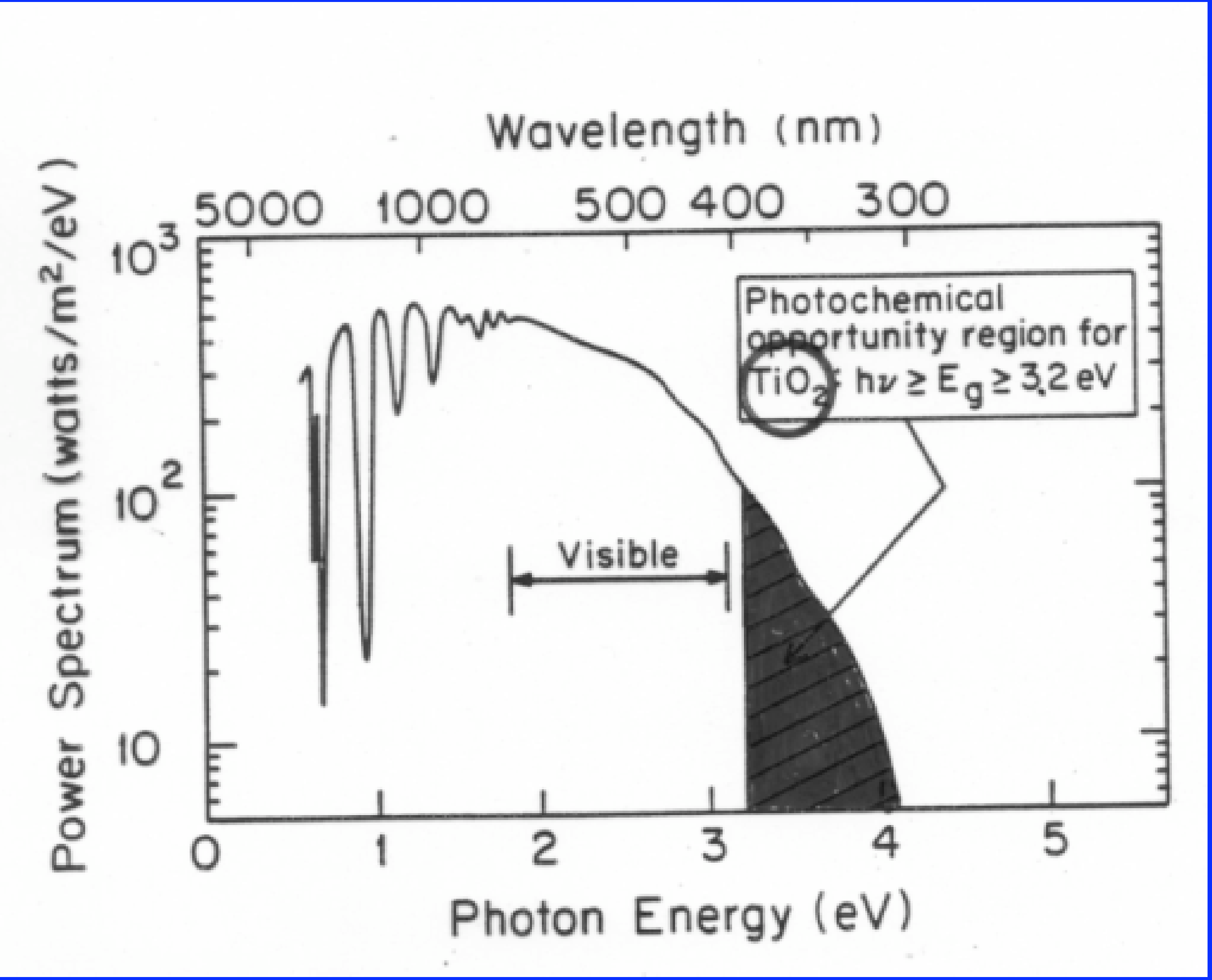
Schematic Multifunctional Film Structure for CBA Destruction



Problems with Multifunctional Film Coating for CBA Destruction

- Polyurethane polymer-anchored enzyme will be destroyed by TiO_2 due to free radical attack as well as directly by UV radiation √
- TiO_2 only activated by UV portion of sunlight √

Solar Spectrum at Sea Level with Sun at Zenith

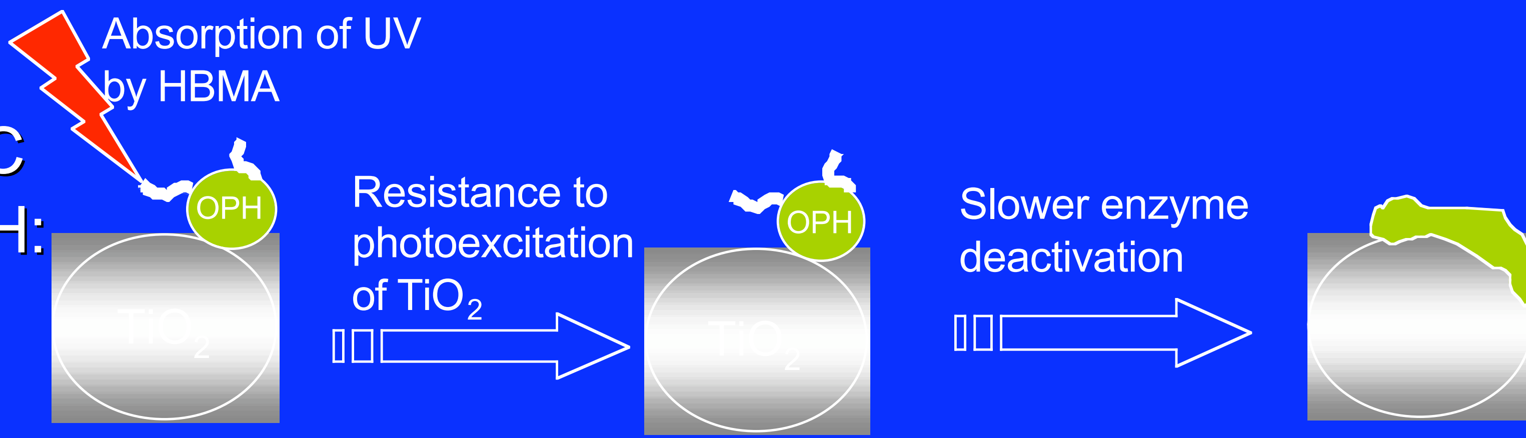


Research Highlight

Alan J. Russell Group, University of Pittsburgh

GOAL: Elucidate mechanism of TiO_2-UV induced enzyme deactivation and rationally design stabilized OPH conjugates.

SCIENTIFIC APPROACH:



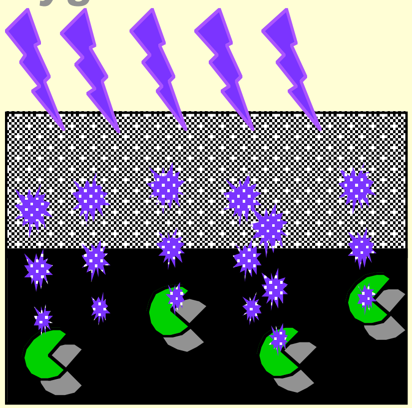
RESULTS: Modified OPH enzyme is stable more than week against TiO_2-UV in coating as well as in solution.

Research Highlight

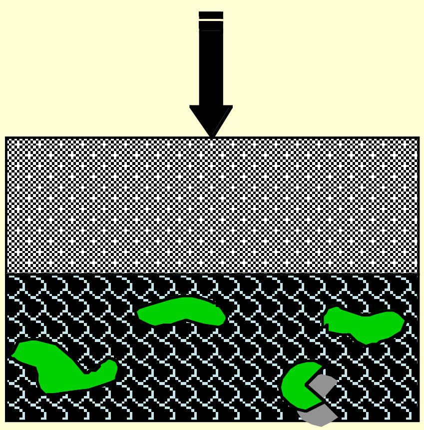
Eric Beckman Group – University of Pittsburgh

PROBLEM

TiO_2-UV generate reactive oxygen radicals

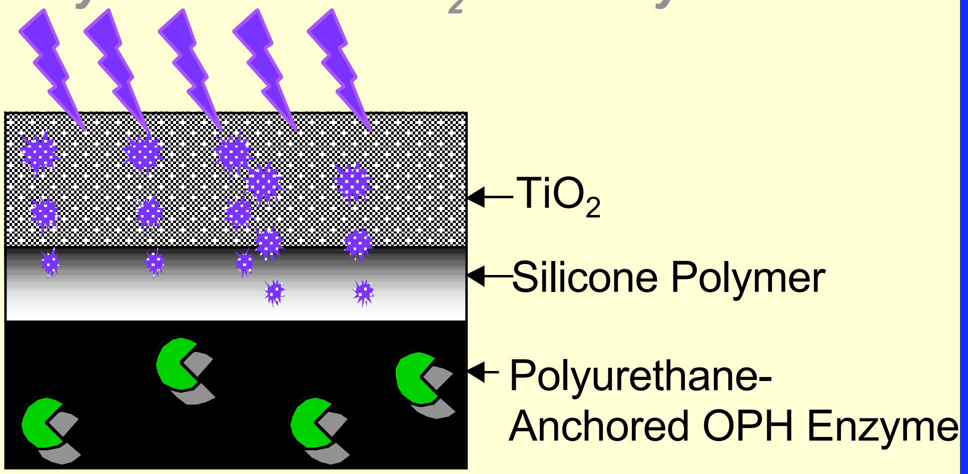


Radicals oxidize enzyme as well as polymer coating

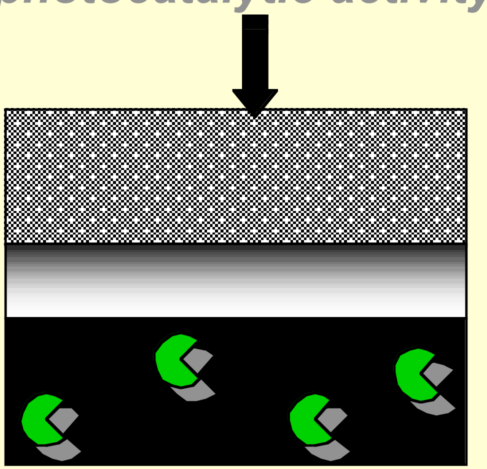


STRATEGY

Oxidation resistant protective layer between TiO_2 and enzyme



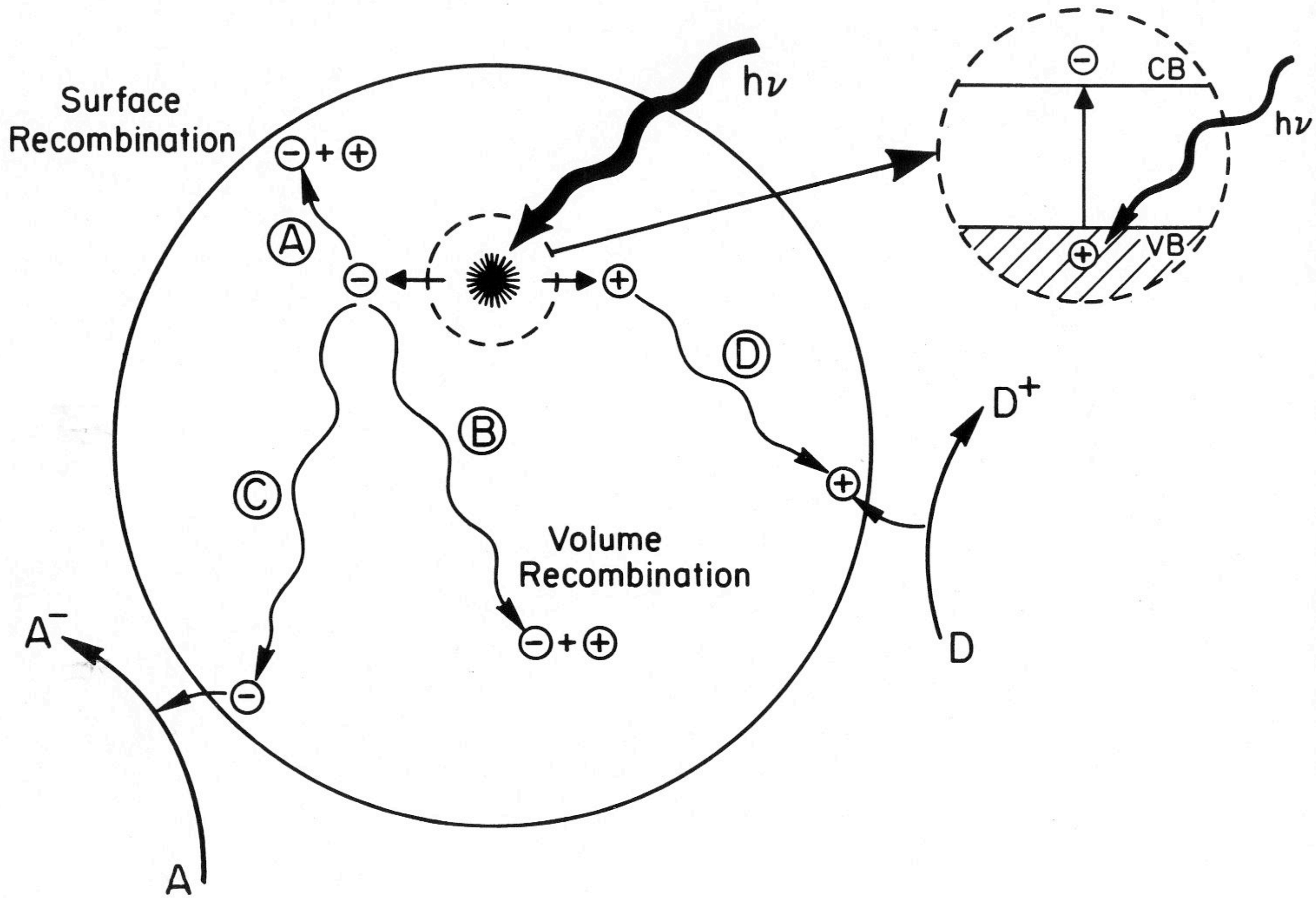
Maintain enzyme & photocatalytic activity



Photochemistry on Titanium Dioxide Surfaces

Decon Downunder, February 2005

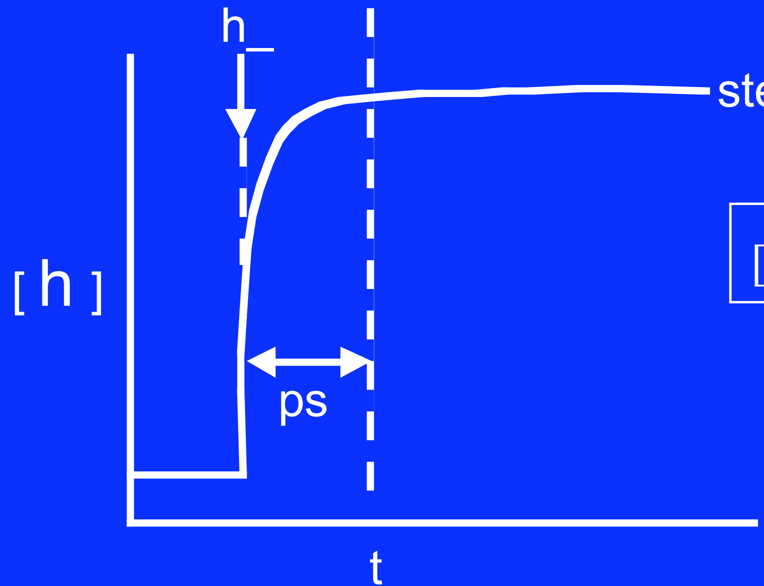
SCHEMATIC PHOTO-EXCITATION IN A SOLID FOLLOWED BY DE-EXCITATION EVENTS



Photochemistry on TiO_2

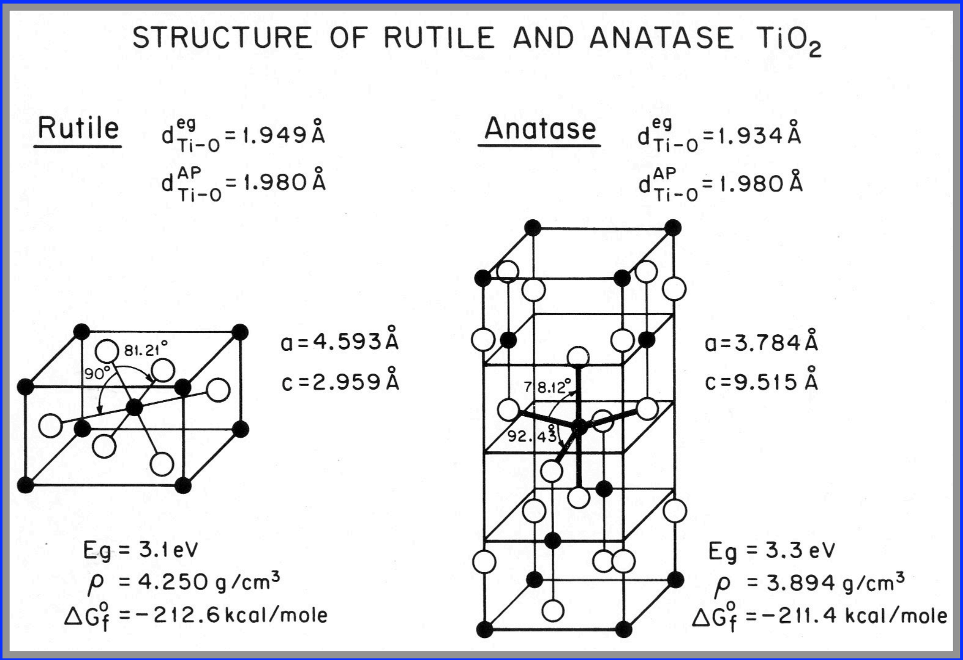
$$TiO_2 + h\_ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} e + h \;;$$

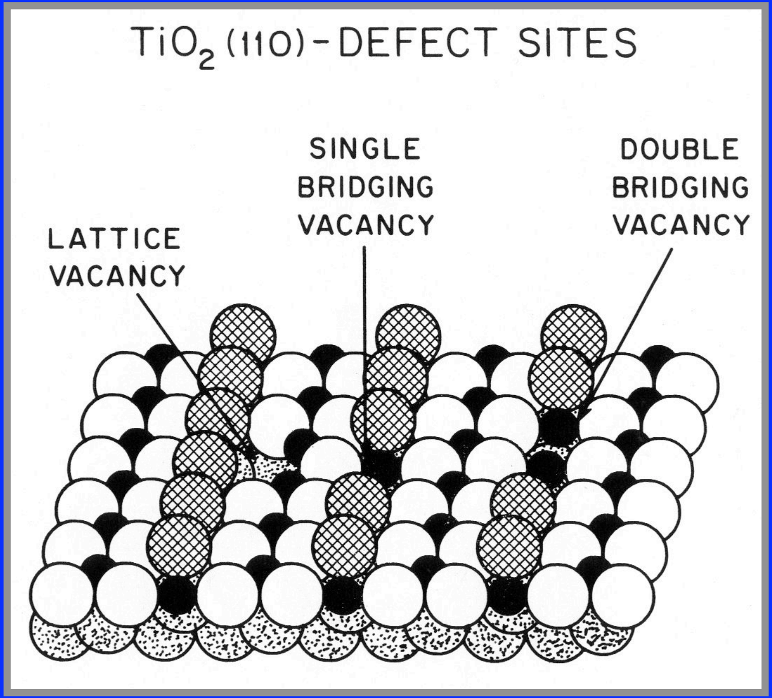
$$h + \text{organic} \xrightarrow{O_2} \text{oxidized organic} \xrightarrow[O_2]{h} \ldots \underbrace{CO_2 + H_2O + \ldots}_{\text{Mineralization products}}$$



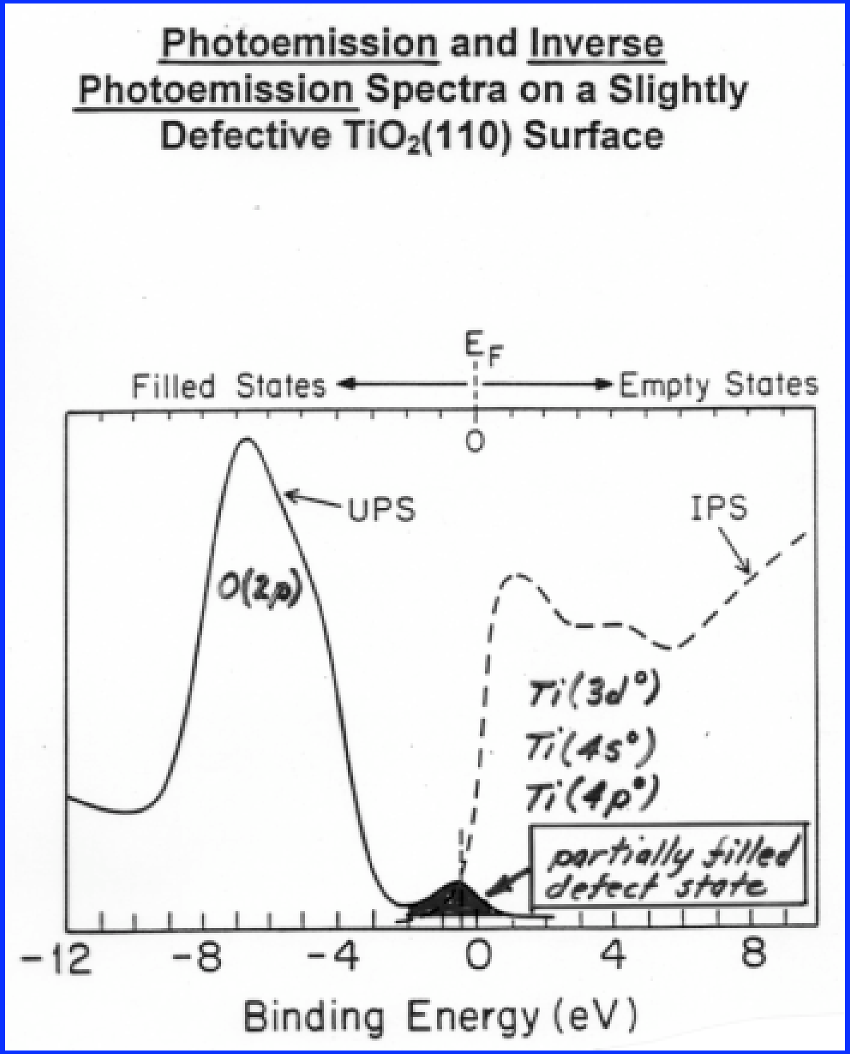
$$\boxed{[h]\_\ F_{h\_}^{1/2}}$$

TiO_2 as a Photochemical Substrate





Heating TiO_2 above ~ 700 – 800 K → O-vacancy defects (reduced TiO_2)



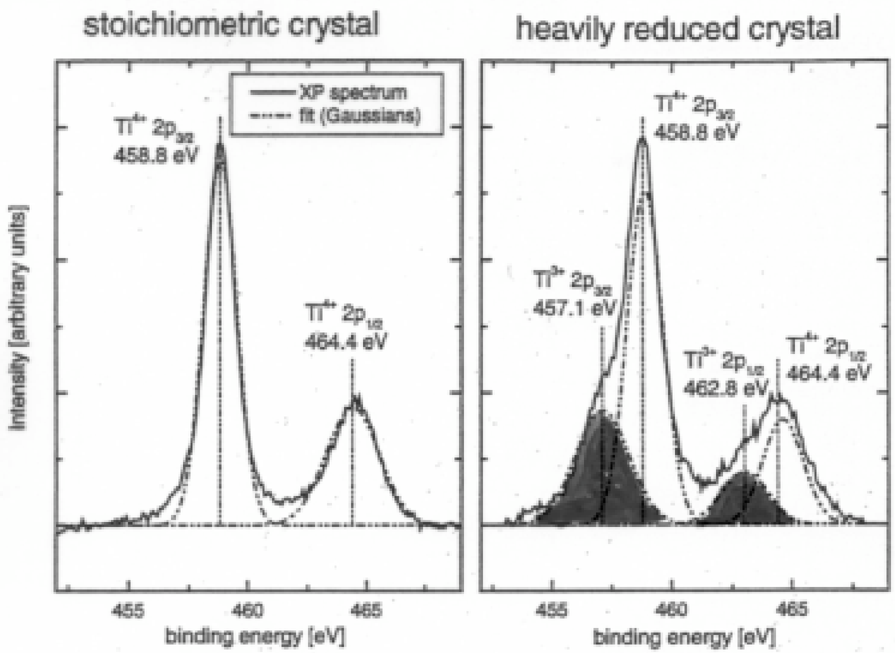
R.A. Bartynski, et al.

JVST A10, 2591 (1992)

Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2 4p^0$

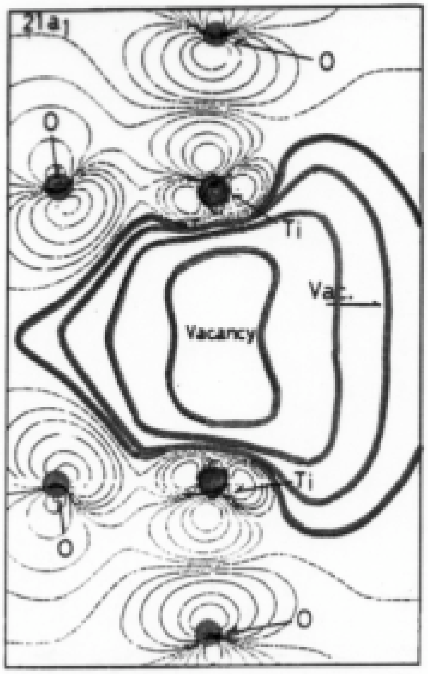
Ti^{+4}: $1s^2 2s^2 2p^6 3s^2 3p^6 \boxed{3d^0 4s^0 4p^0}$

XPS Evidence for TiO_2 Reduction by Heating



S. Reiβ, H. Krumm, A. Niklewski, V. Staemmier, Ch. Wöll, *Journal of Chemical Physics* 116, 7704 (2002)

HOMO: O-Vacancy Defect Site - $SrTiO_3(100)$



● 16% Ti (3d)
● 41% Ti (4p)
● 43% Ti (4s)

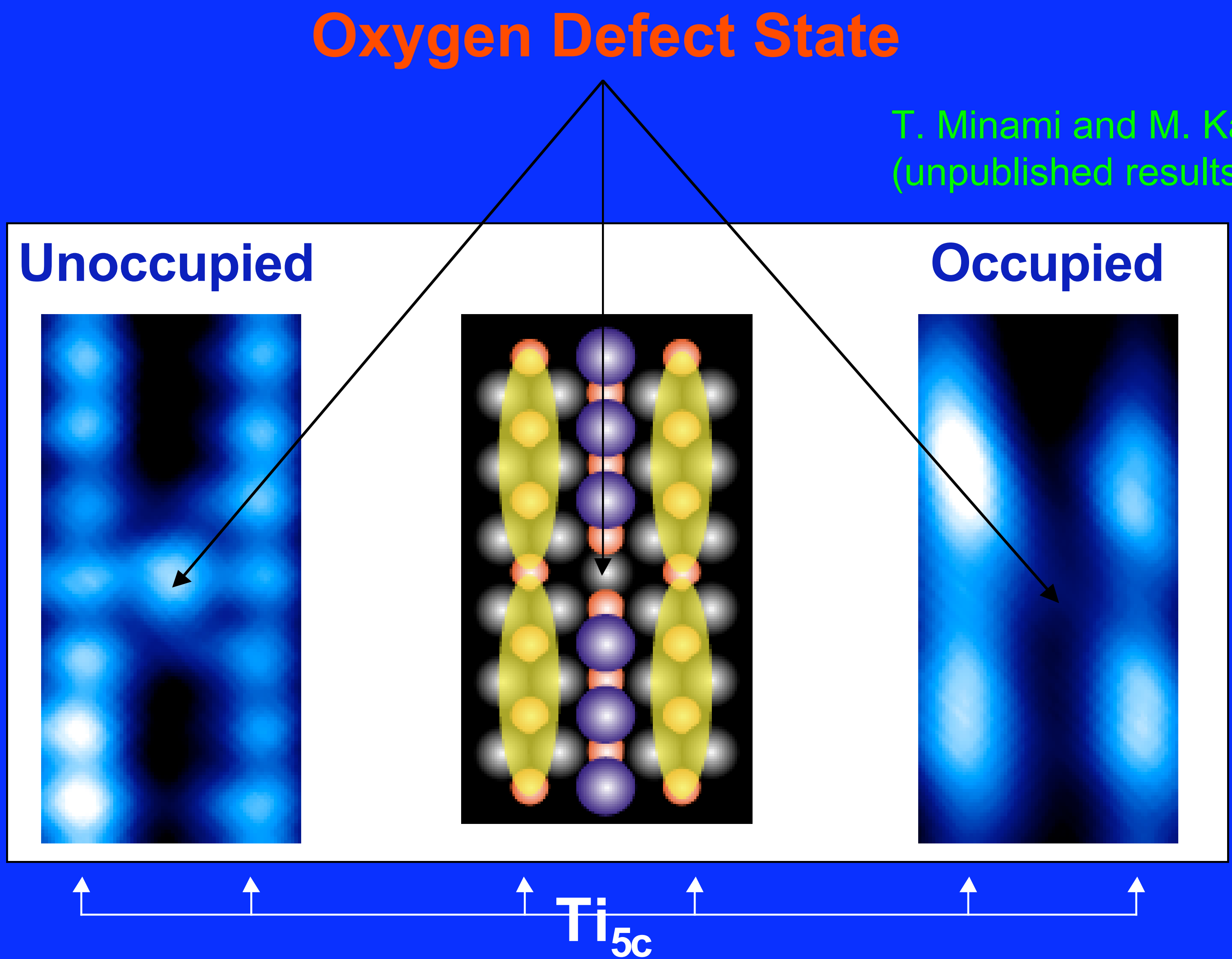
M. Tsukada, H. Adachi and C. Satoko,
Prog. Surf. Sci. 14, 113 (1983).

A More Recent Look at Electronic Structure of Oxygen Defects/TiO_2(110)

STM - STS

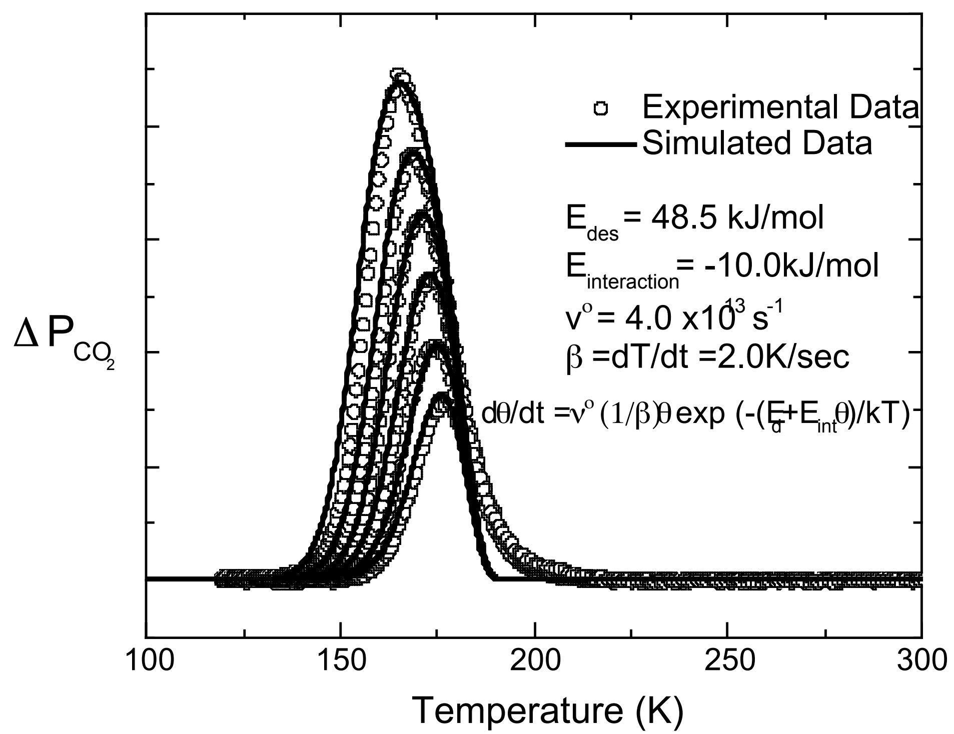
Spatial distribution of Ti 3d state

T. Minami and M. Kawai
(unpublished results)

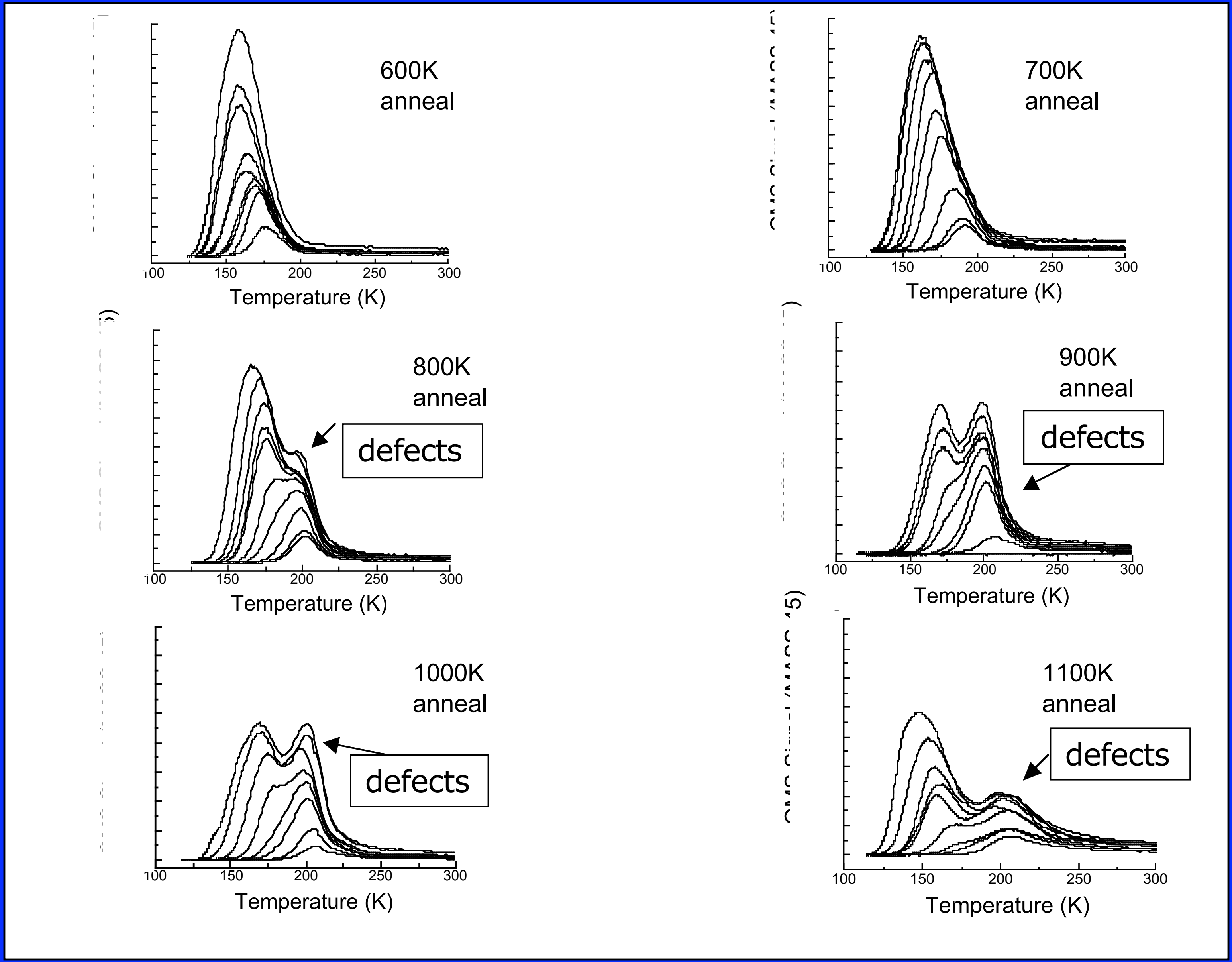


Use of CO_2 Adsorption to Detect Surface Defect Sites Produced by Heating

Comparison of Experimental and Simulated $^{13}CO_2$ Desorption Spectra on $TiO_2(110)$ – Fully Oxidized Surface

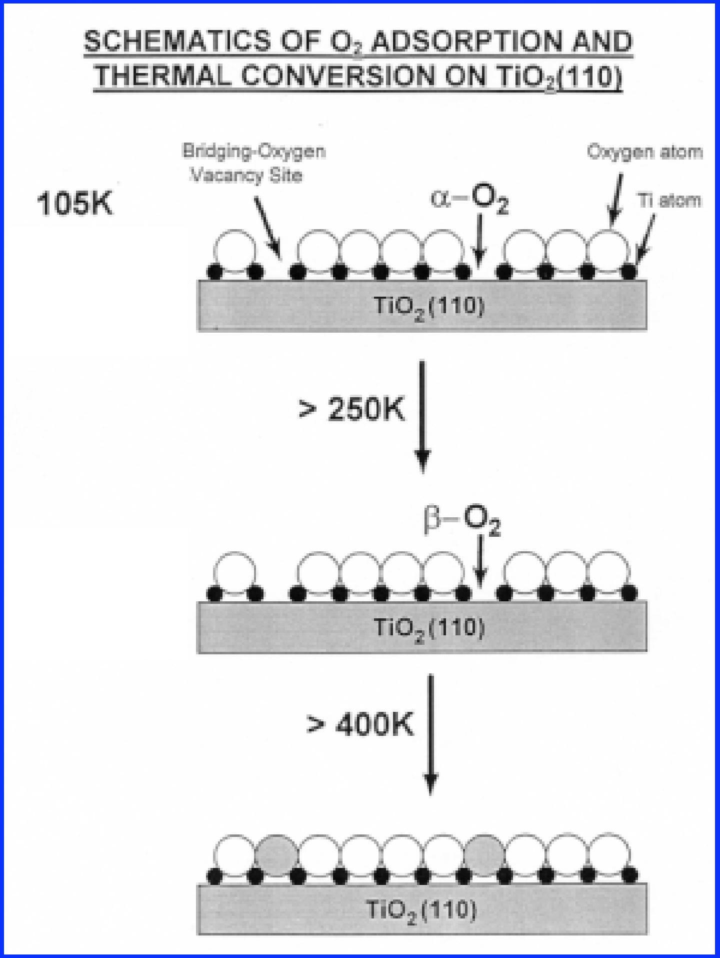


Successive Reduction of TiO_2(110) Using CO_2 to Detect Vacancy Defect Sites

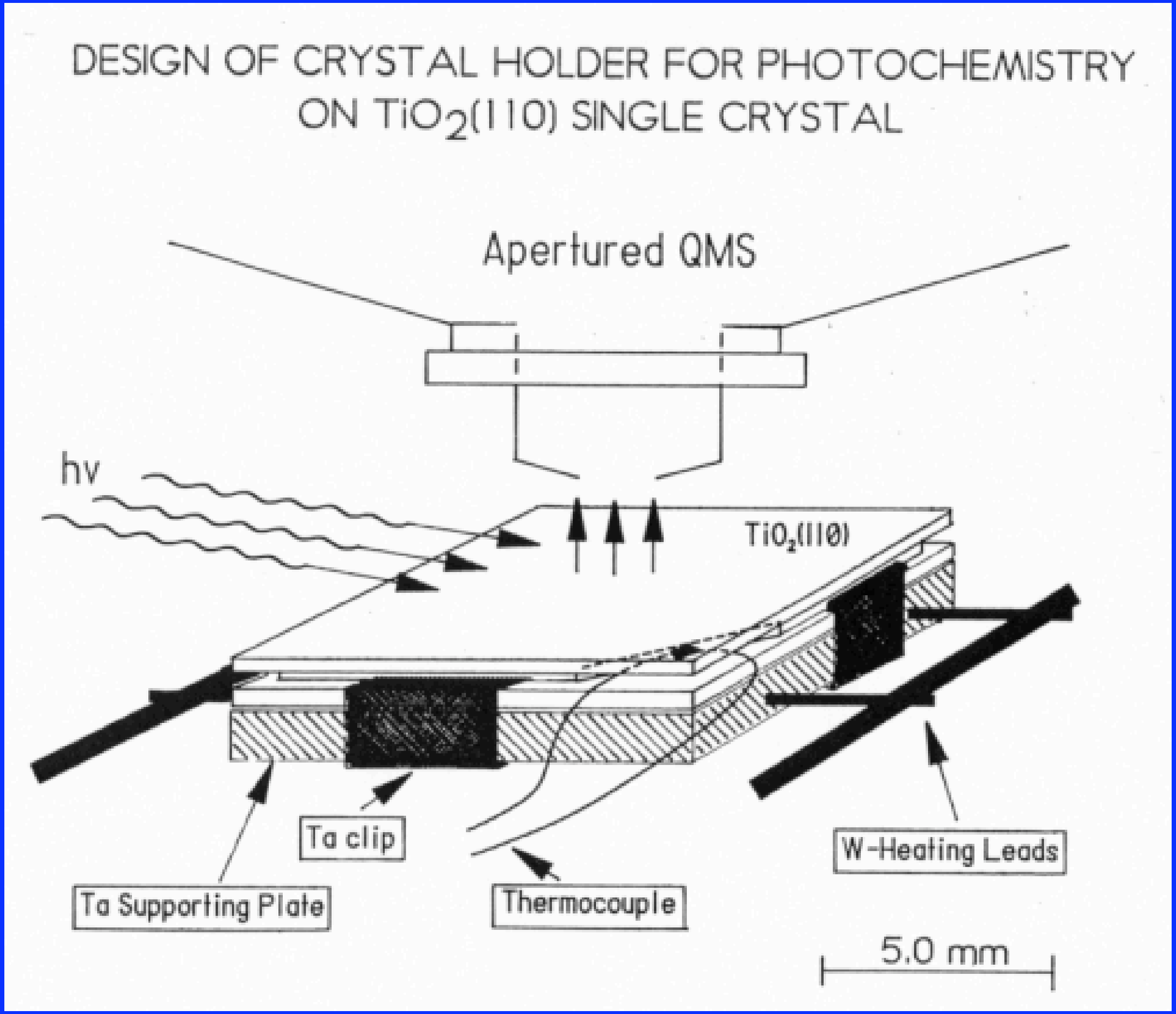


T. L. Thompson, O. Diwald and J. T. Yates, Jr.
J. Phys. Chem. B **107** (2003) 11700.

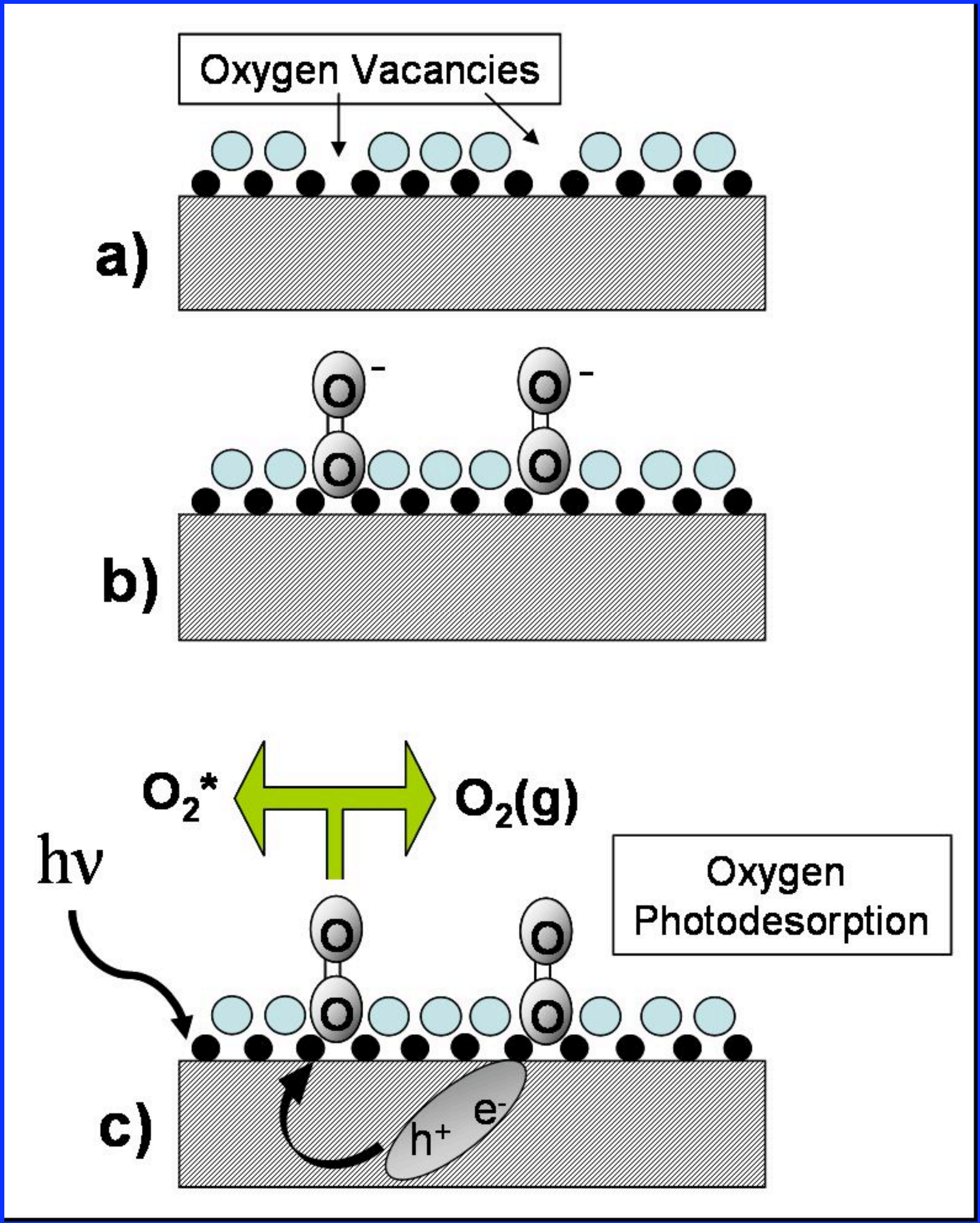
Chemisorbed O_2 on TiO_2(110) Vacancy Defect Sites



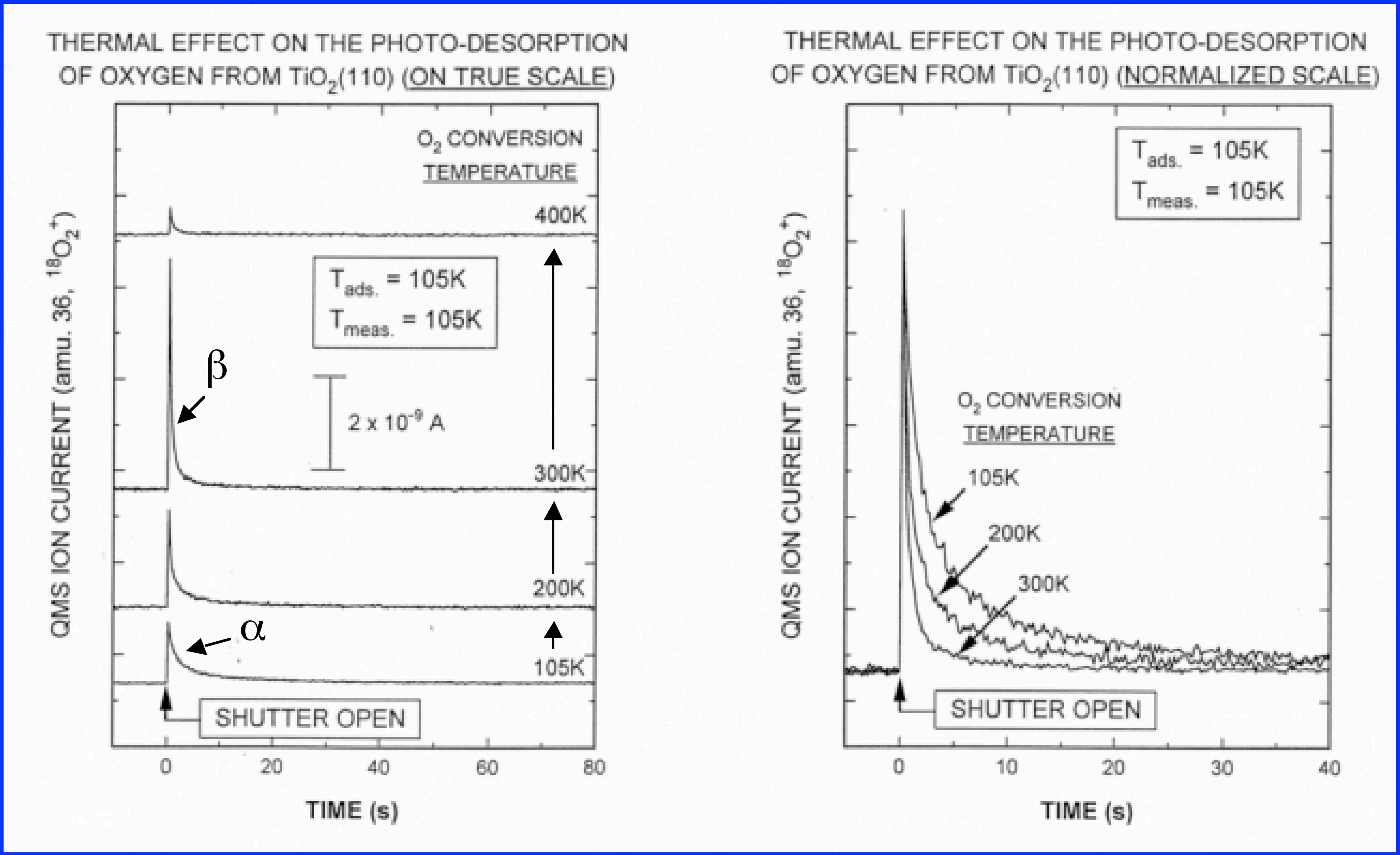
Detection of Photodesorption of O_2



Model for the Photoinduced Desorption of Molecular Oxygen



Thermal Conversion: α-O_2 → β-O_2



α-O_2 and β-O_2 – Exhibit Distinctly Different Surface Photochemistries

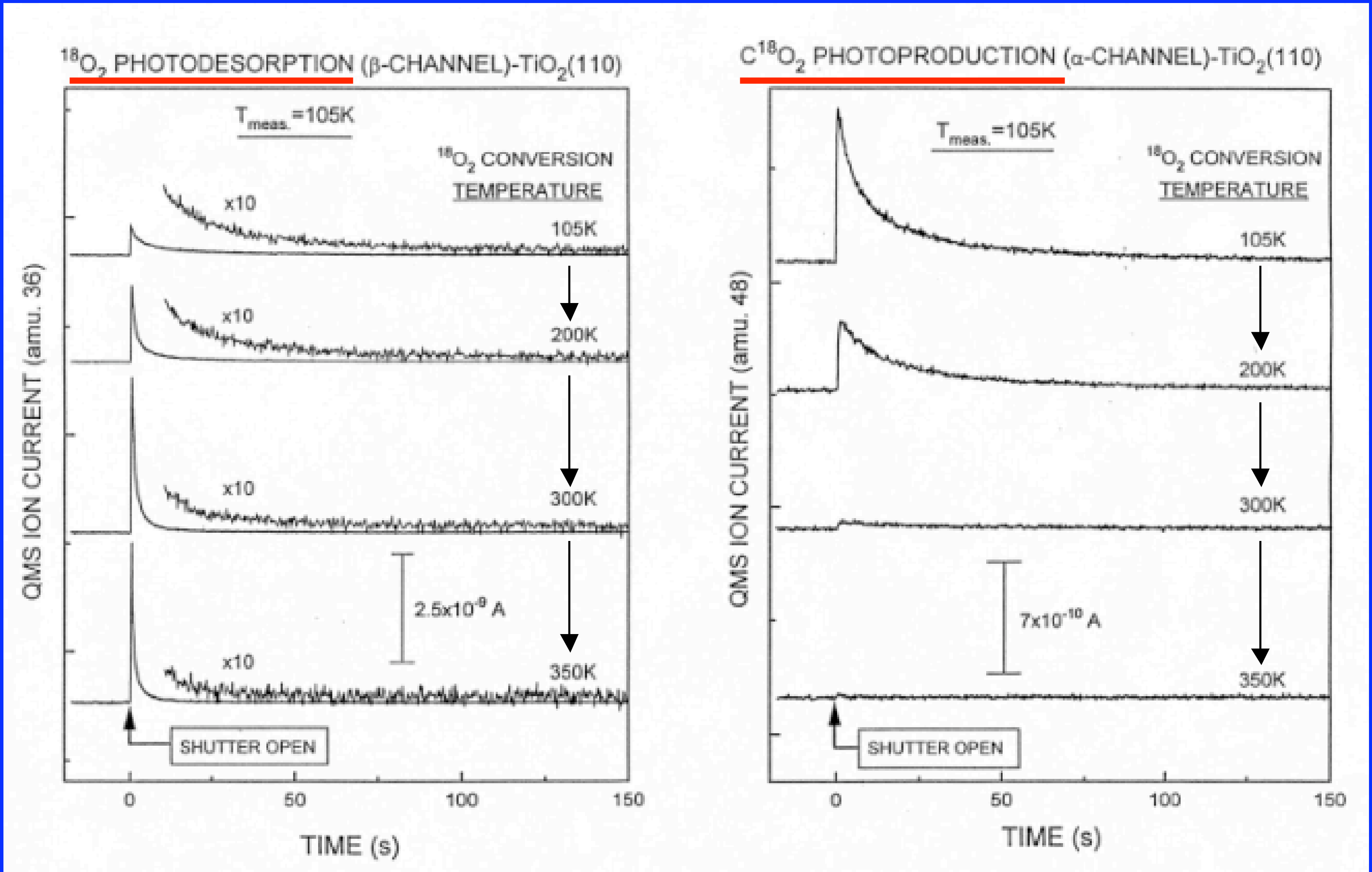
- α-O_2 + hv $\rightarrow$ O_2(g)

  $\rightarrow$ also causes oxidation of CO $\rightarrow$ CO_2

- β-O_2 + hv $\rightarrow$ O_2(g) only

G. Lu, A. Linsebigler and J.T. Yates, Jr., J. Chem. Phys. 102, 3005 (1995)

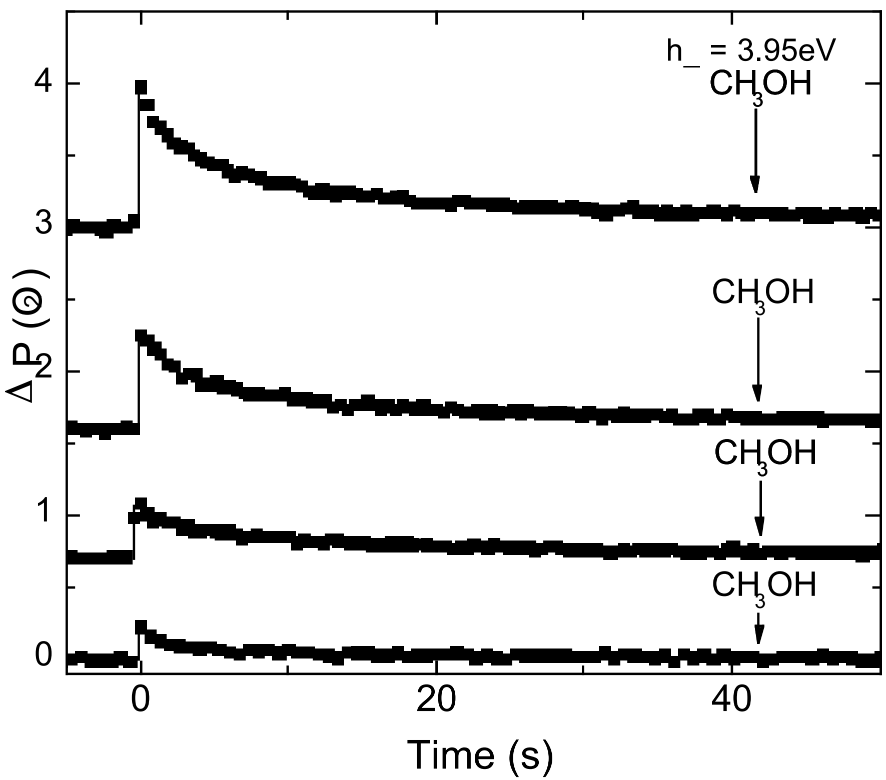
Observation of α-O_2 and β-O_2 Surface Photochemistries



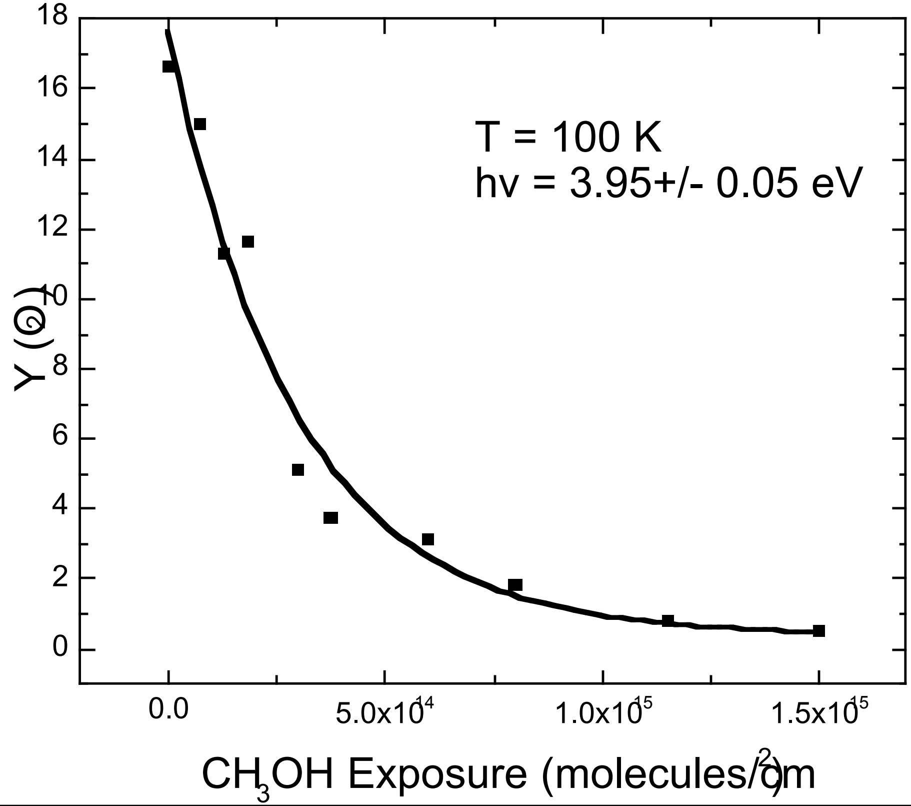
We can manipulate the photogenerated holes in TiO_2 using hole scavenger molecules.

Role of Hole Scavengers on O_2 Photodesorption – CH_3OH (a) + h _ CH_3O (a) + H^+

O_2 Photodesorption

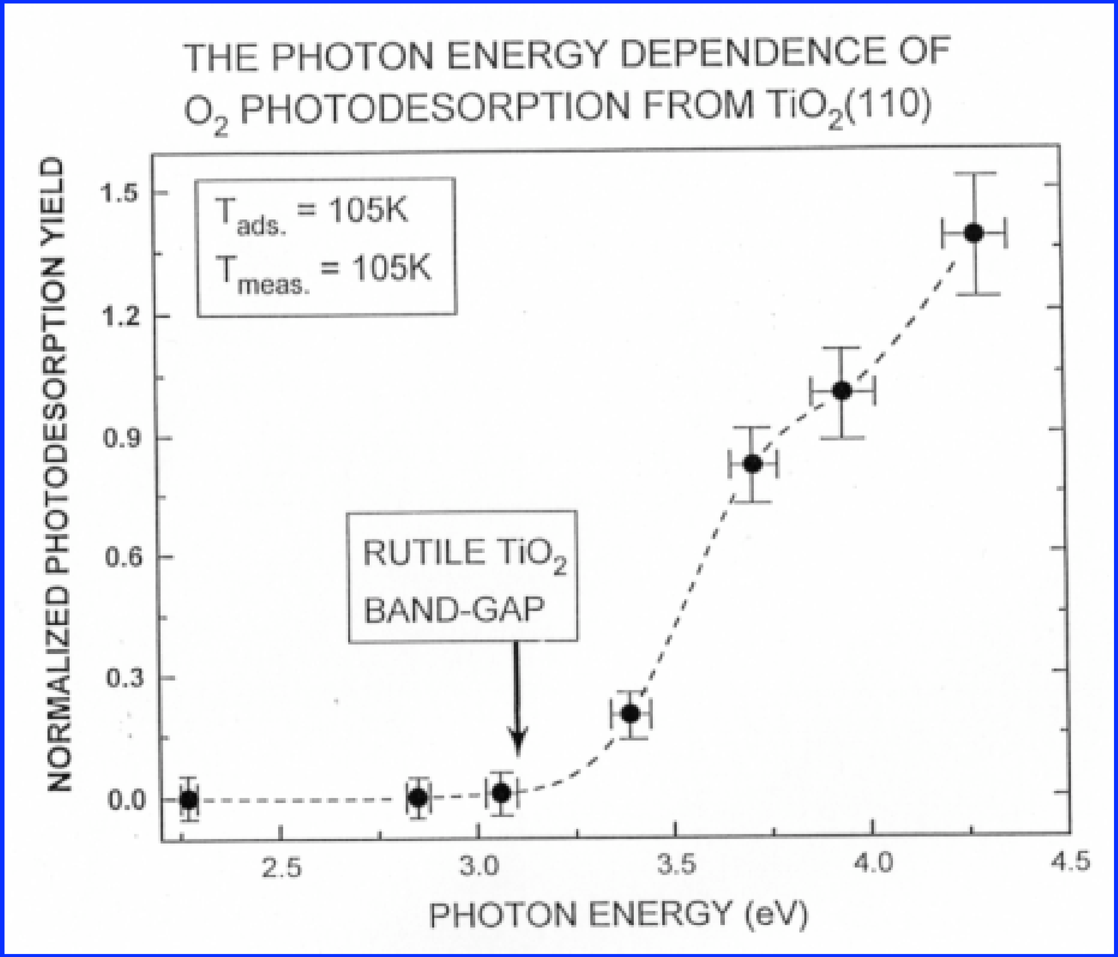


Yield of O_2(g)



Tracy L. Thompson and John T. Yates, Jr.
(to be published)

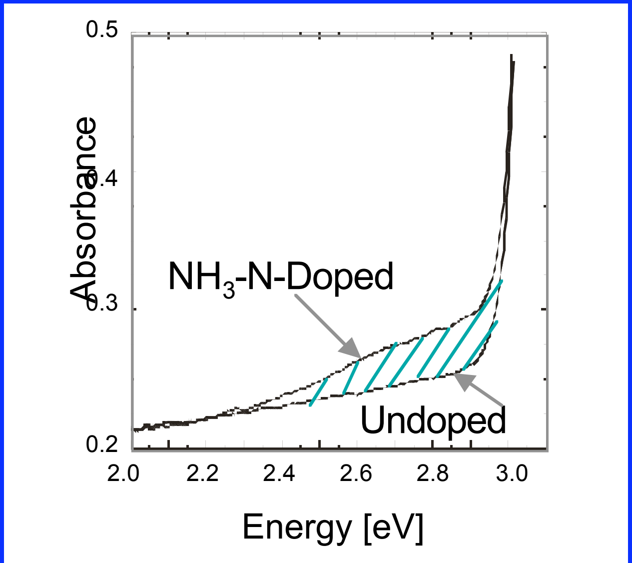
Photon Energy Dependence for Photodesorption: α-O_2



Nitrogen Doping of TiO_2 to Lower Photon Threshold Energy for Photooxidation

- A major goal of project is to extend photo activity into visible spectral region of sunlight.

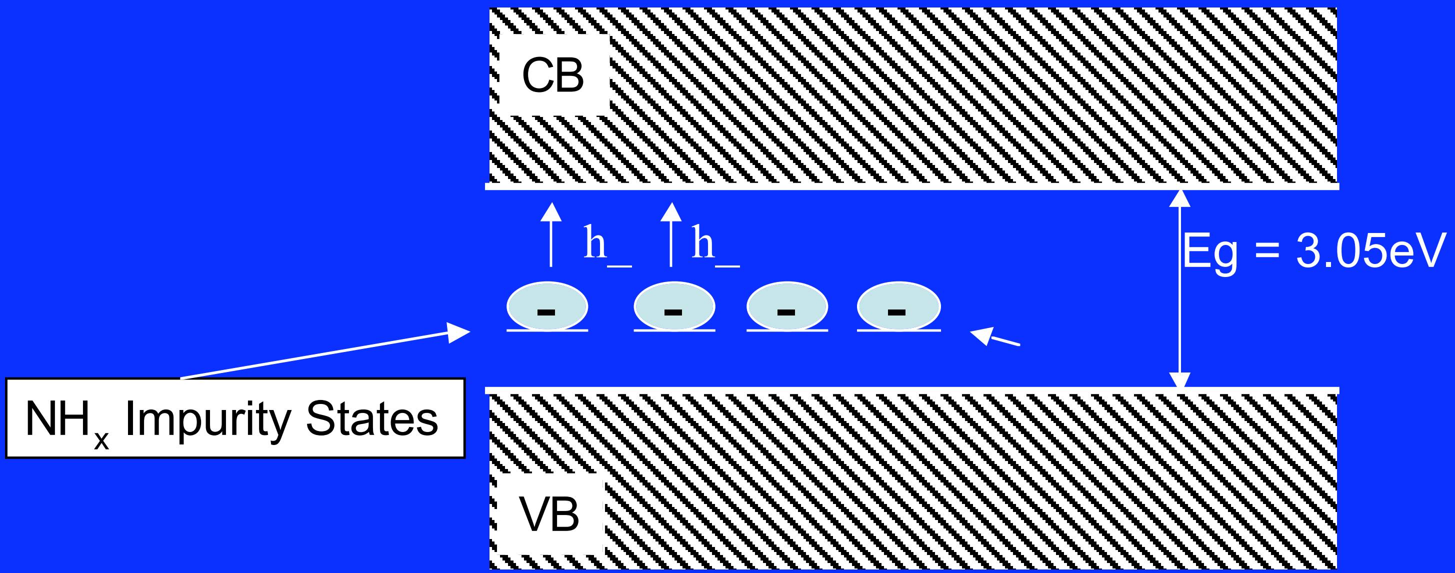
- $NH_3(g) + TiO_2(110) \xrightarrow{870K}$ green color



O. Diwald, T. Thompson, T. Zubkov, E. Goralski, S. Walck, and J.T. Yates, Jr. *J. Phys. Chem. B* 108 (**2004**) 6004-6008.

- Note that absorption band extends to h_ = 2.4 eV threshold

NH_x Doping of $TiO_2(110)$ – Lowering Photothreshold Energy

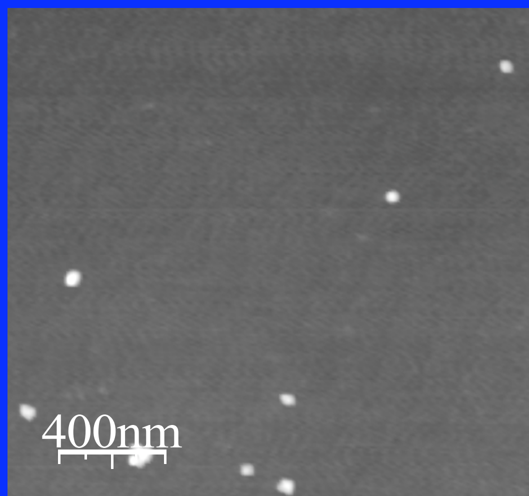


Shift of Photoexcitation Threshold by NH_3 Doping

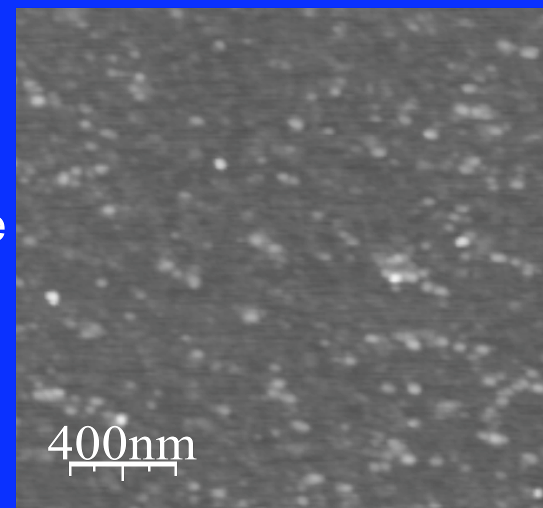
Use of $Ag^+(aq) + TiO_2(110) + h\_ \longrightarrow Ag^\circ$ to Measure NH_3-N-Doping Effect

Ag Photoreduction on $TiO_2(110)$ h_ = 2.47 eV

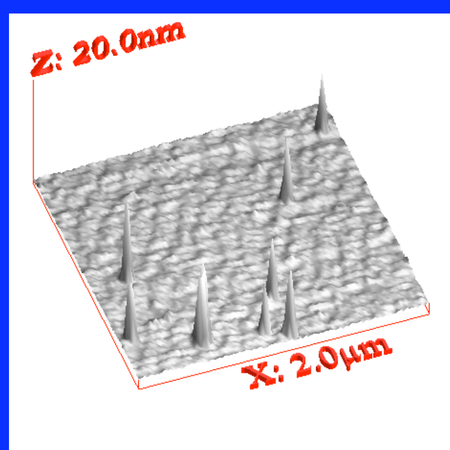
Undoped

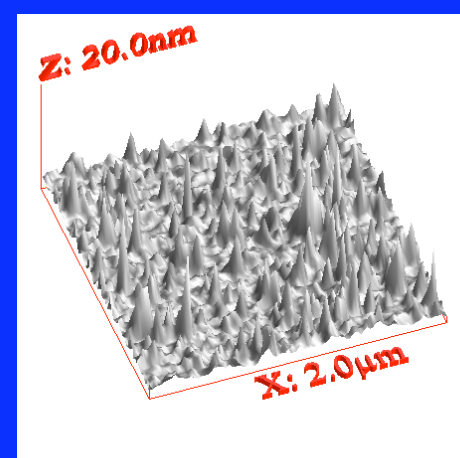


AFM Probe



NH_3-N-Doped



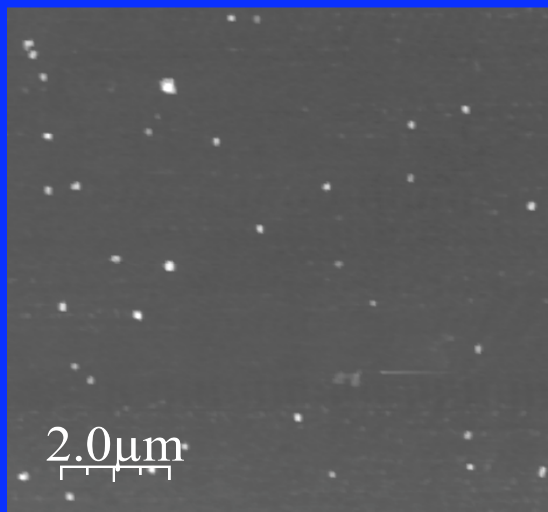


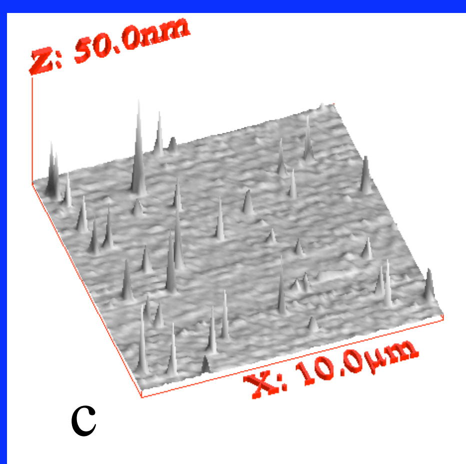
Shift of Photoexcitation Threshold by NH_3 Doping

Ag Photoreduction on TiO_2(110)

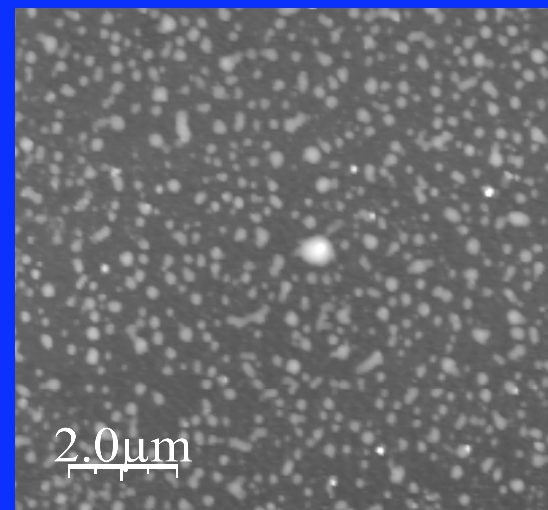
h_ = 2.98 eV

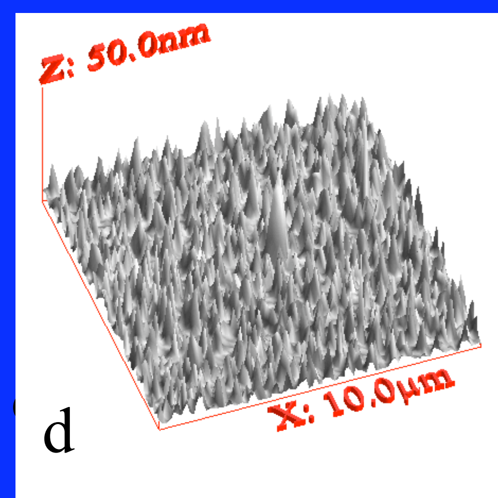
Undoped





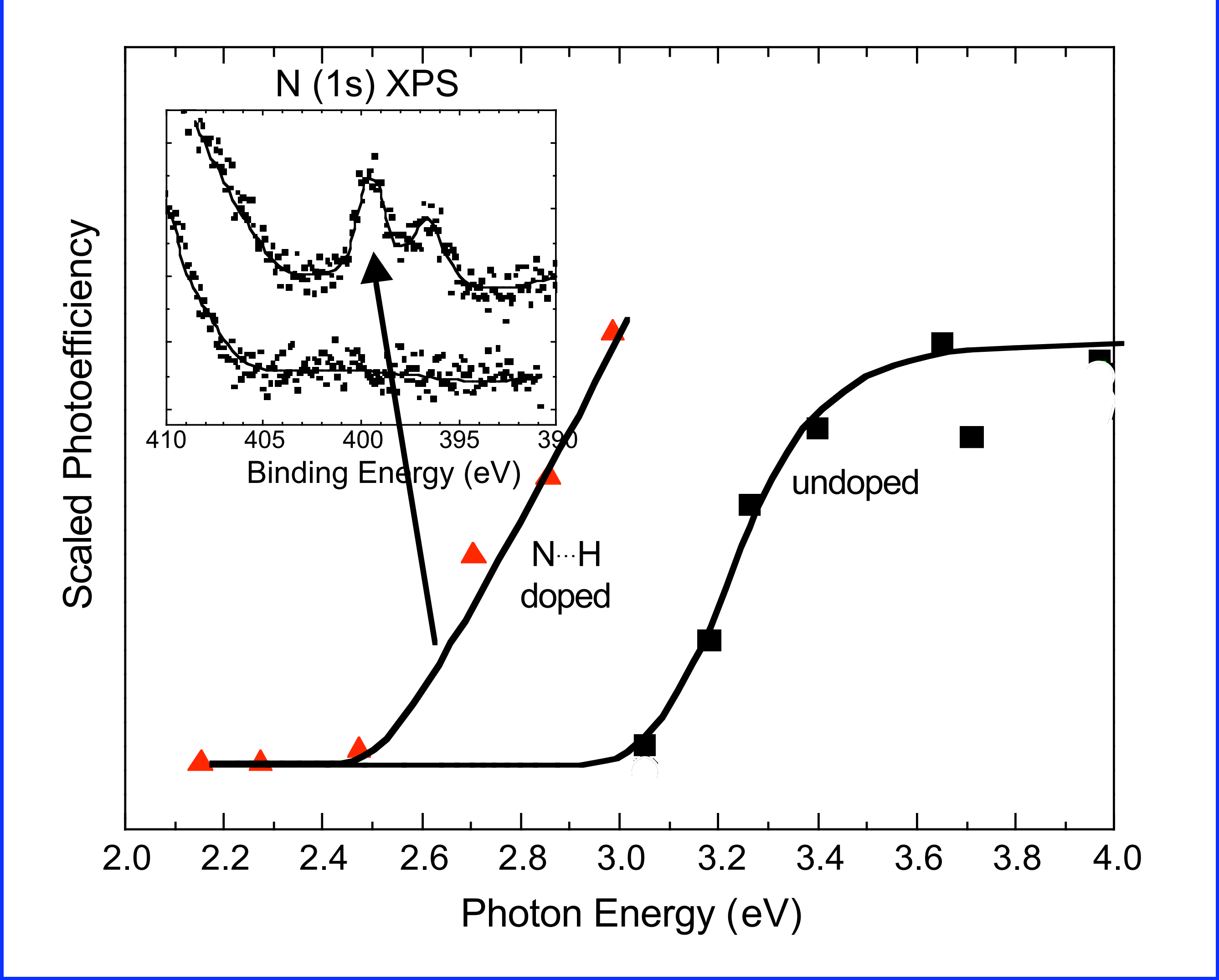
NH_3-N-Doped



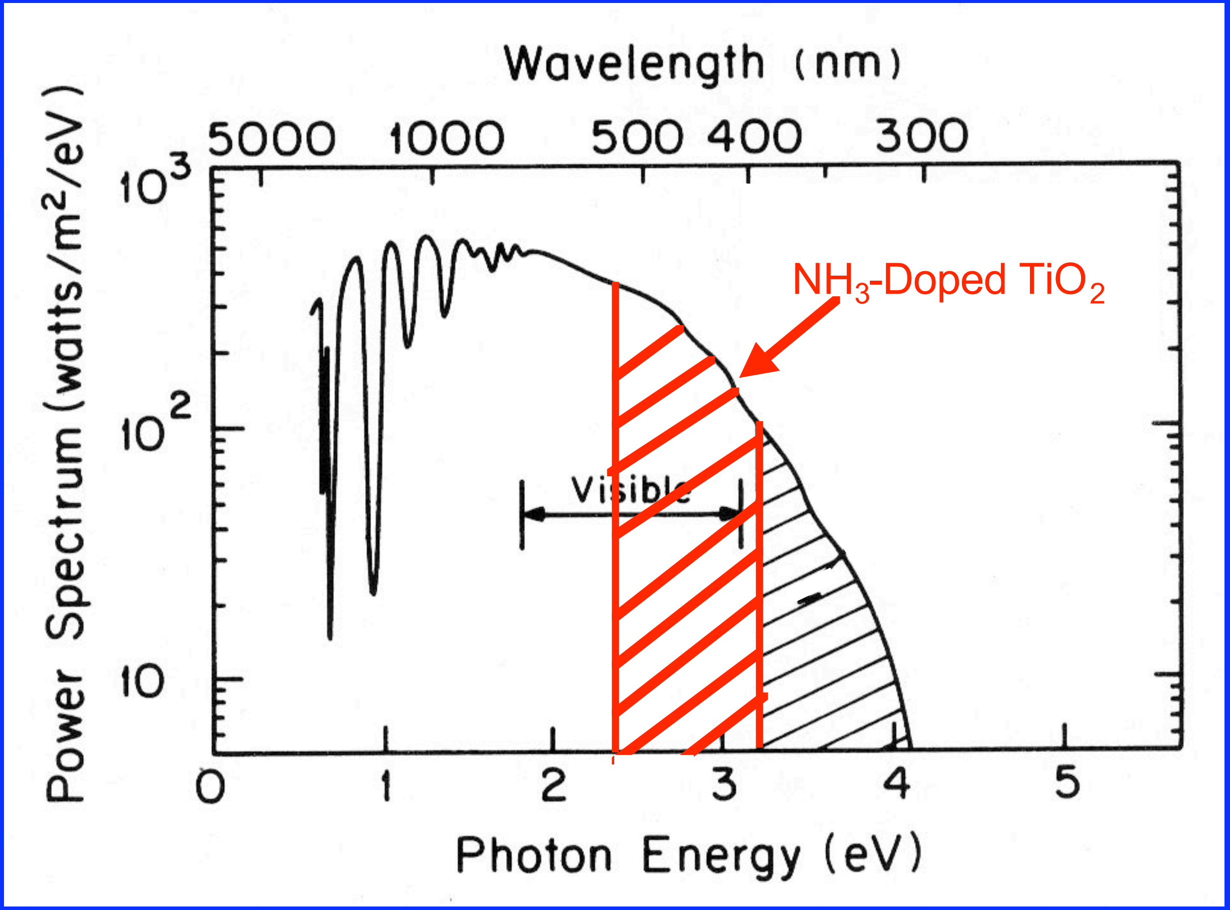


Action Curve for Photoinduced Ag-Deposition on $TiO_2(110)$

Effect of Nitrogen Doping on $TiO_2(110)$ Photoefficiency



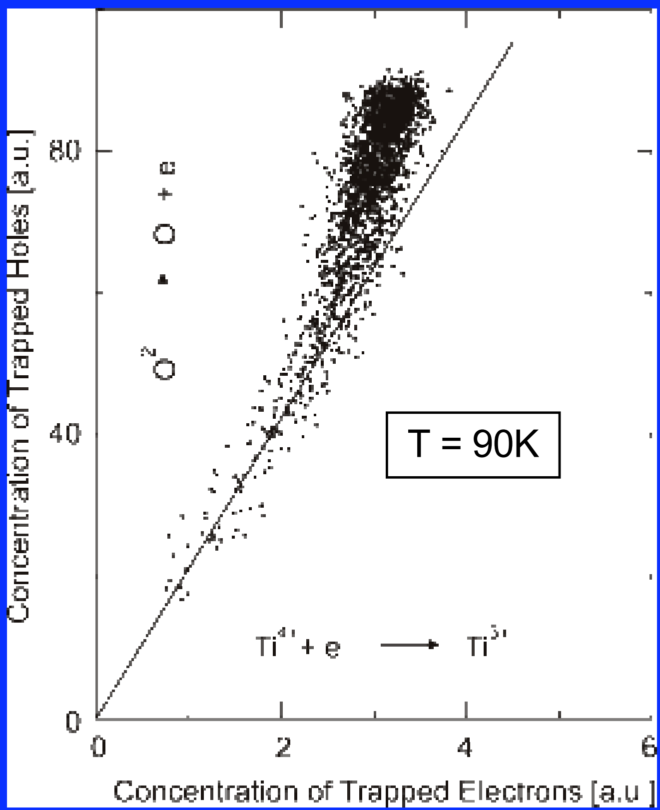
Shift of Photoexcitation Threshold by NH_3 Doping

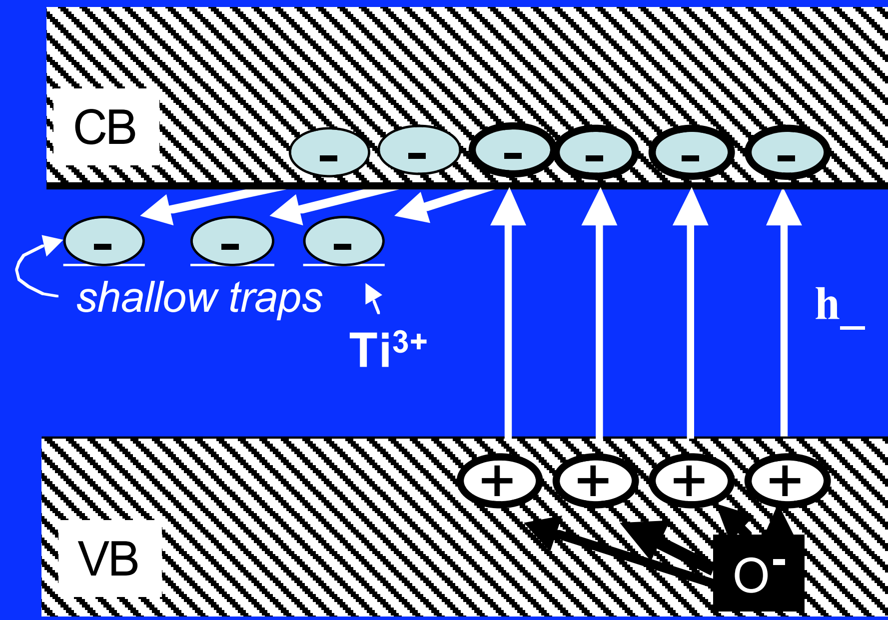


Studies on TiO_2 Powder

- ESR
- IR

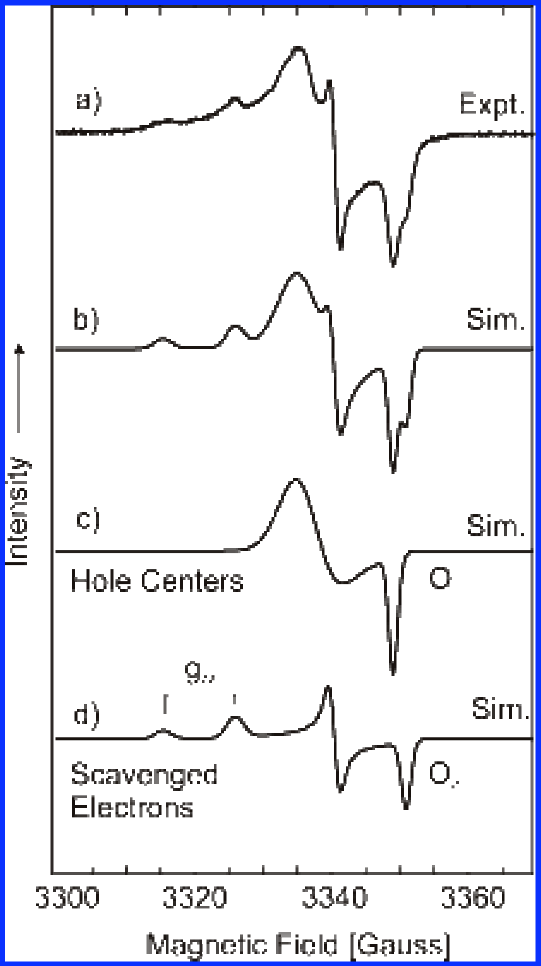
Correlation between Trapped Electrons and Holes





T. Berger, M. Sterrer, O. Diwald, E. Knözinger,
D. Panayotov, T. L. Thompson and J. T. Yates, Jr.
Accepted for publication, J. Phys. Chem. B

O_2 (a) as an Electron Scavenger: Production of O_2^- (ads.)



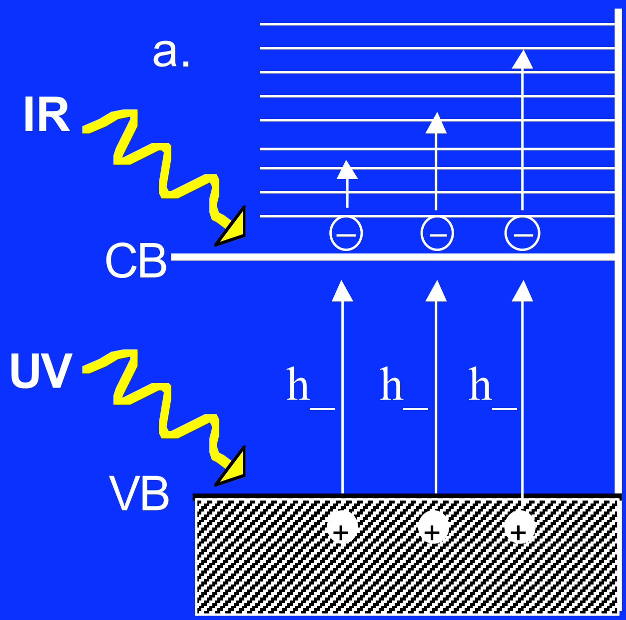
$TiO_2 + O_2(a)$

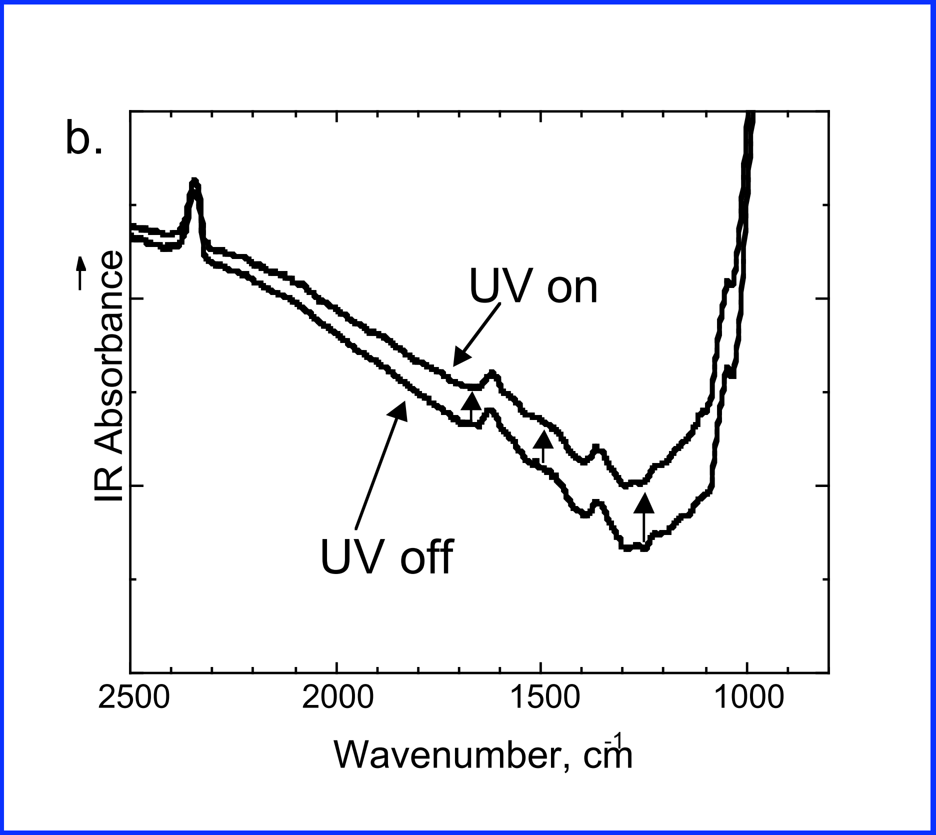
h_

lattice O^- (hole)
+
scavenged e (O_2^-(a))

IR Spectroscopy Can Be Used To See Electrons Excited Into Conduction Band

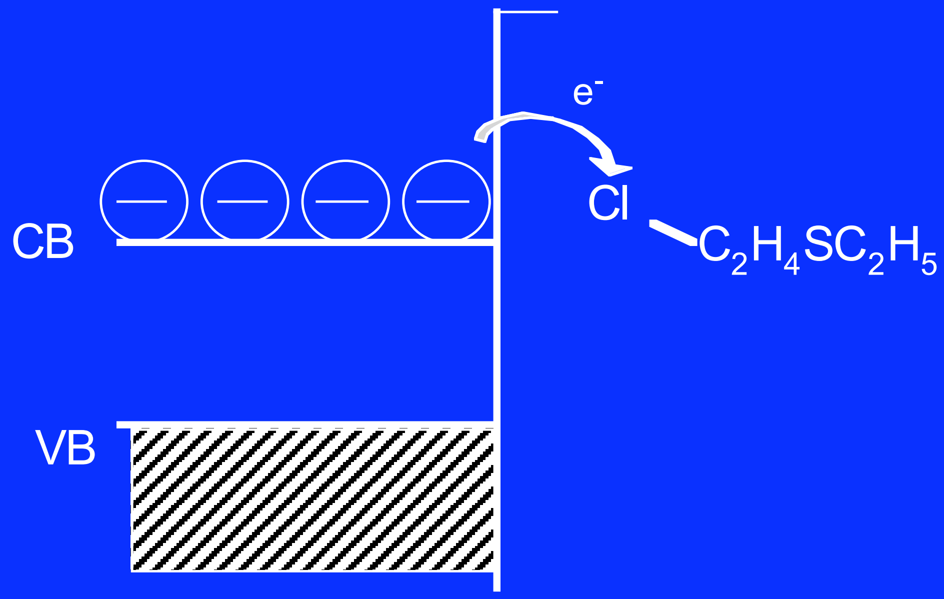
UV-Induced Increase of IR Background – CB Trapping



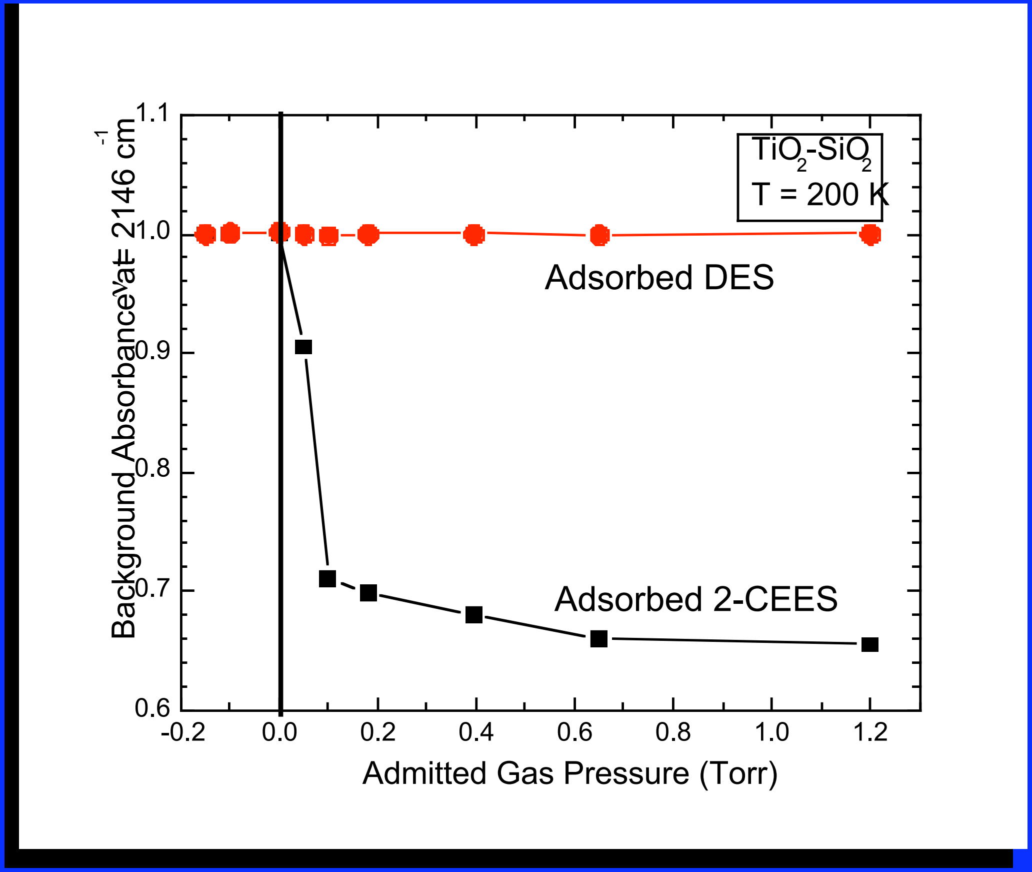


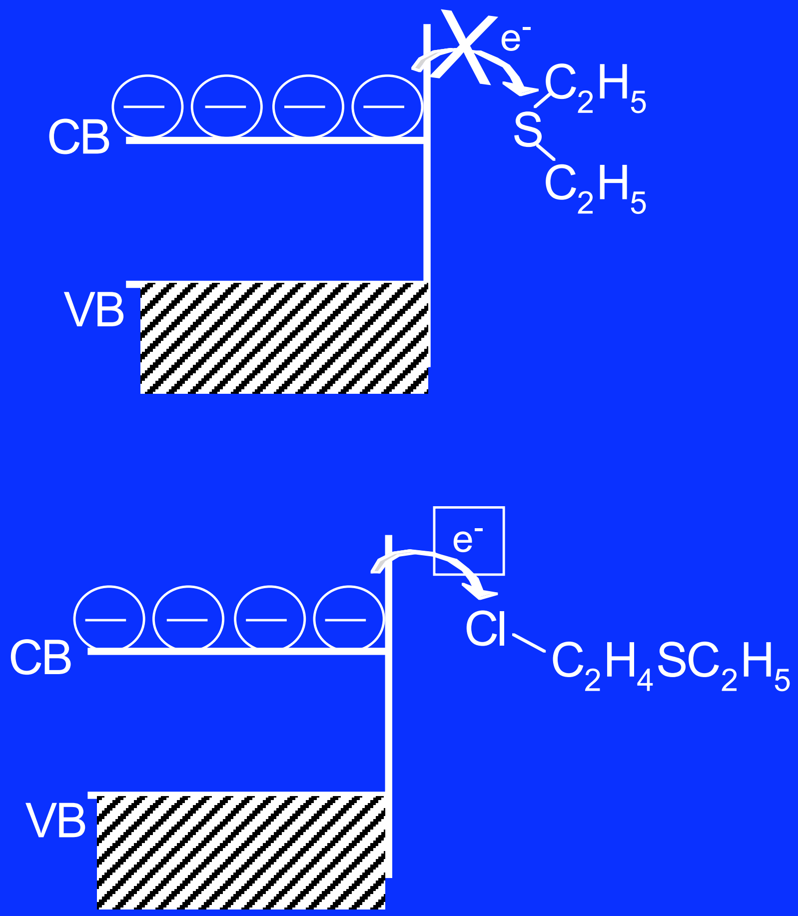
T. Berger, M. Sterrer, O. Diwald, E. Knözinger,
D. Panayotov, T. L. Thompson and J. T. Yates, Jr.
Accepted for publication, J. Phys. Chem. B

Conduction Band Electrons Transfer to Adsorbed Organic Molecules



Preferential Electron Transfer:
TiO_2 CB Electrons to Electrophilic Molecules





- **CB electron transfer to electrophilic atom in adsorbed molecules**

SUMMARY – MAJOR FINDINGS

- **Multifunction Polymer-Enzyme-TiO_2 Film**
  - Photodegradation problems being solved
- **O_2 Photochemistry on TiO_2 – Need Defect Sites for O_2 Adsorption**
  - α-O_2 active for photooxidizing organics
  - β-O_2 active for photodesorption only
- **Hole Scavengers**
  - Suppress β-O_2 photodesorption

- Extension of TiO_2 Photoactivity into Visible Solar Spectral Range – NH_3 Doping

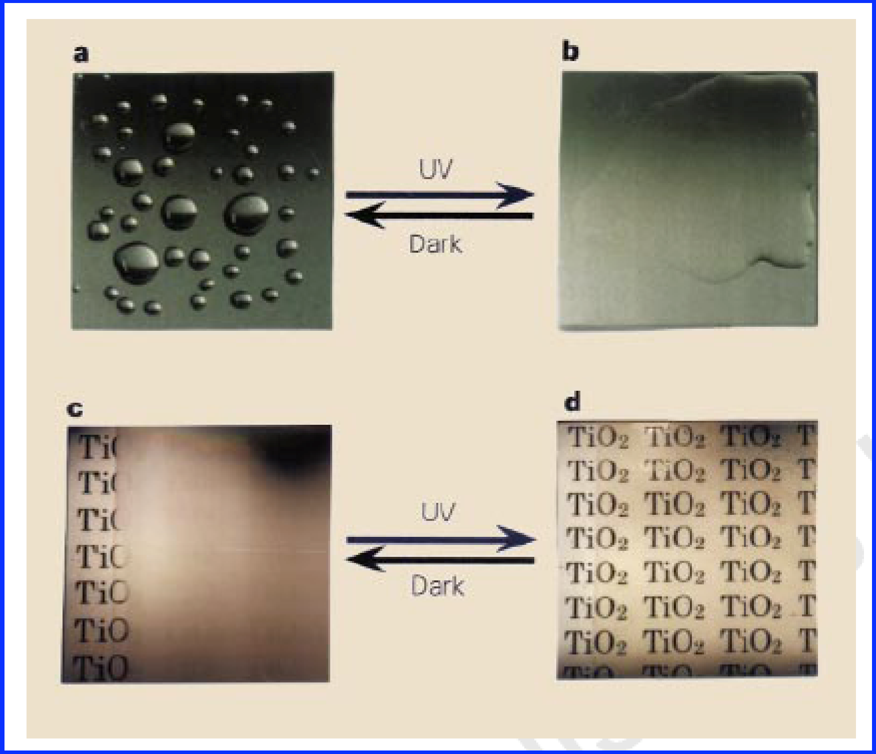
- ESR Detects 3 Excited Species Made by Photoexcitation of TiO_2
  - O^{1-} hole
  - Ti^{3+} trapped electron
  - O_2^- trapped electron on O_2(a)

- IR Detects Trapped Electrons in CB

- Electron Transfer from CB Occurs to Most Electronegative Atom in an Adsorbed Molecule (2-CEES)

A Recent Development- Explanation of UV-Induced TiO_2 Hydrophilicity

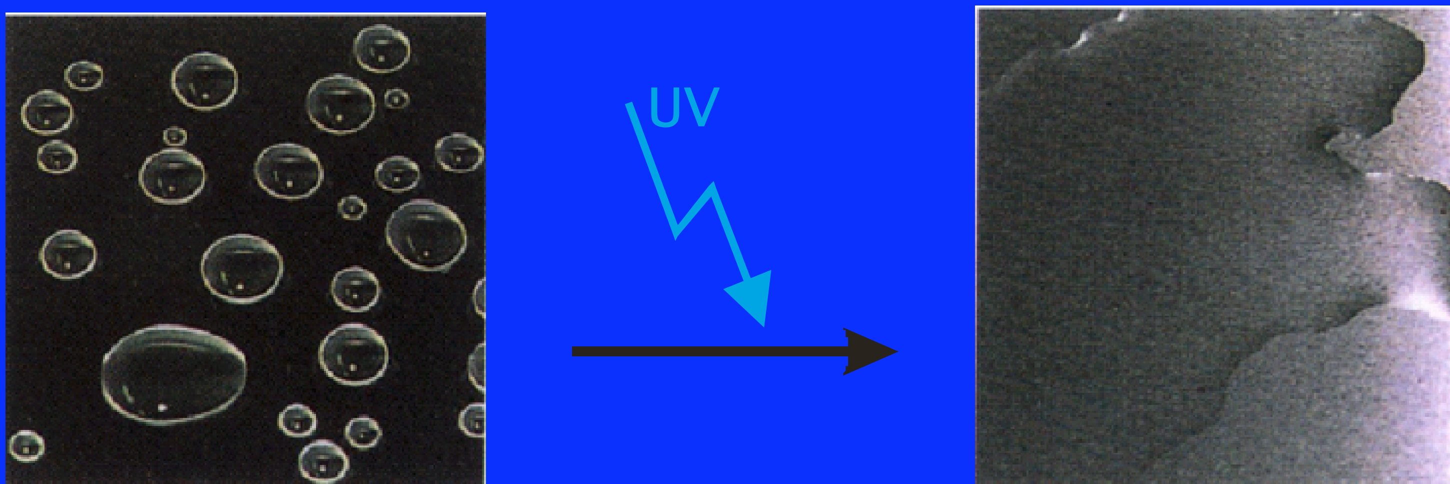
“Light-Induced Amphiphilic Surfaces”



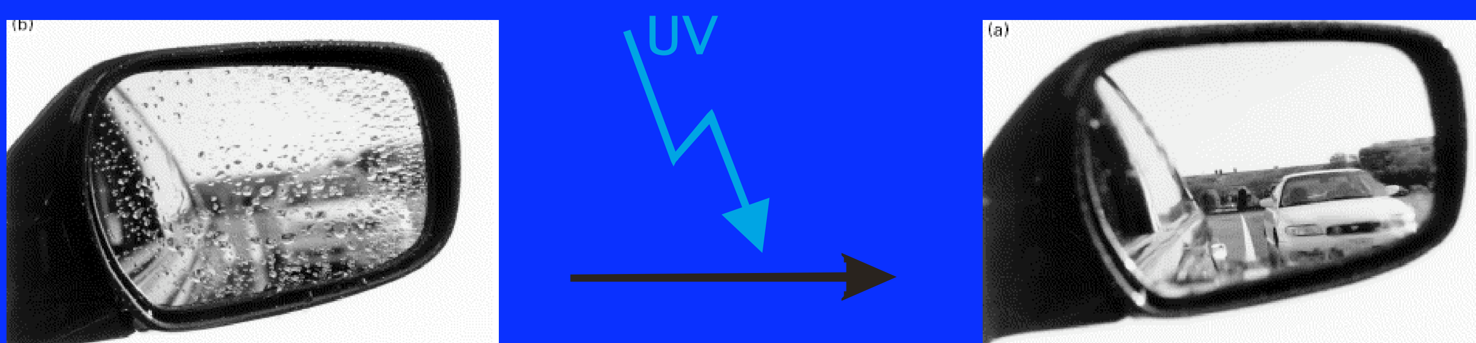
Rong Wang, Kazuhito Hashimoto, Akira Fujishima, Makota Chikuni, Eiichi Kojima, Atsushi Kitamura, Mitsuhide Shimohigoshi, Toshiya Watanabe

Nature, **388** (1997) 870-873.

TiO_2 - UV-induced Hydrophilicity - Applications
Anti-fogging



Taken from: Fujishima, Hashimoto, Watanabe, "TiO_2-Photocatalysis, Fundamentals and Applications", BKC Inc. Tokyo, 1999



Taken from: Hata, Kai, Yamanaka, Oosaki, Hirota, Yamazaki, JSAE Review 21, 97-102, 2000

60% of Toyota automobiles already use this technology today.

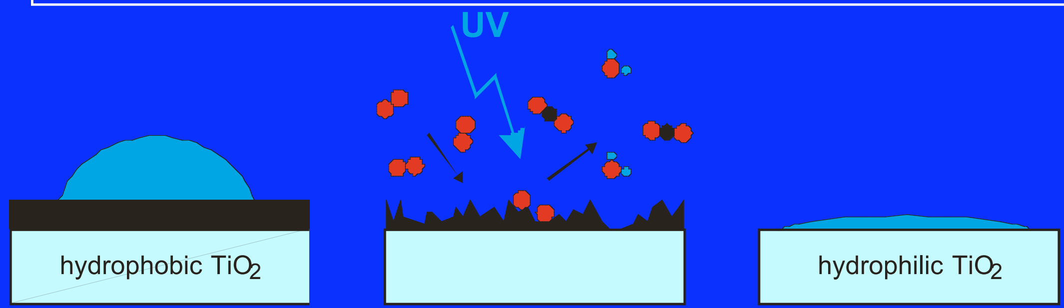
SUNCLEAN™
Self-Cleaning Glass by PPG

SunClean self-cleaning glass by PPG is designed to...
MAKE YOUR LIFE EASIER.

What causes TiO_2 to become hydrophilic in UV?

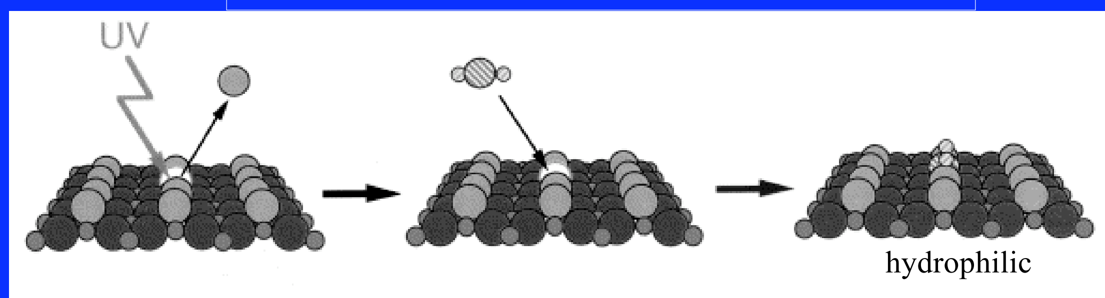
3 Models:

- Photocatalytic removal of organic compounds ?



Fujishima, Rao, Tryk, J. Photochem. Photobio C **1**, 1 2000.

- UV induced oxygen vacancies ?



Nakajima, Koizumi, Watanabe, Hashimoto, J. Photochem. Photobiol. A **146**, 129-132, 2001

- UV-Induced bond breaking?

Sakai, Fujishima, Watanabe, Hashimoto, J. Phys. Chem. B **103**, 2188, 1999.

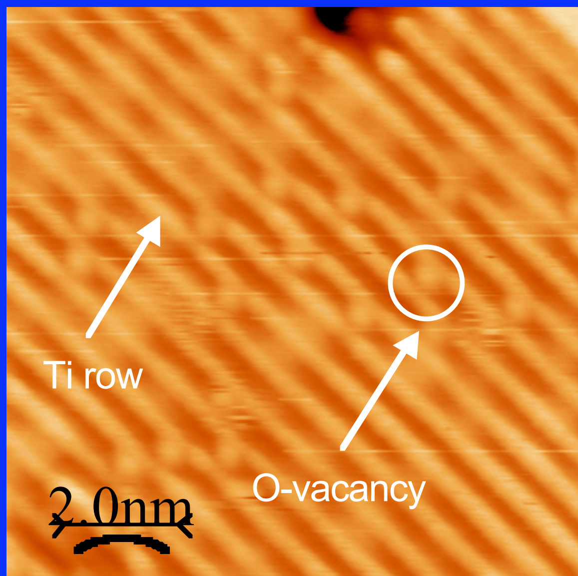
Problems with Existing Understanding of the UV-Induced Hydrophilicity Phenomena on TiO_2

- **All current contact angle measurements have been made in the ambient atmosphere on surfaces which are not atomically clean. Hydrocarbon (and other organic contamination) effects are uncontrolled.**

- **Problem needs a clean surface-ultrahigh vacuum approach and atomic resolution of surface atoms.**

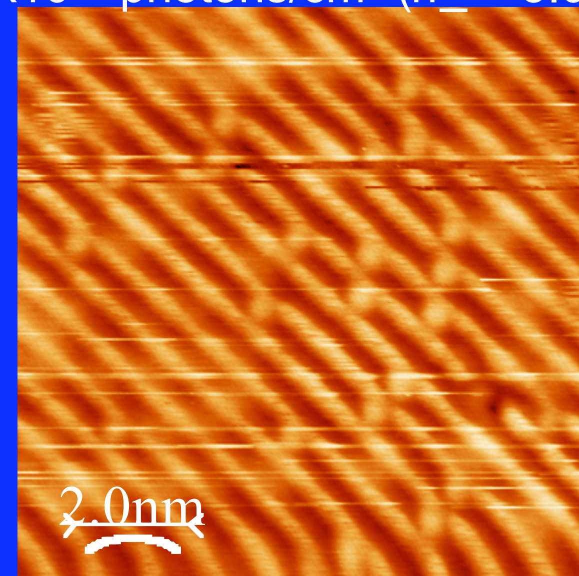
STM Investigation of Vacancy Formation by Intense UV Irradiation – $TiO_2(110)$-(1x1)

No Irradiation



UV Exposure:

5.4×10^{21} photons/cm^2 (h_ > 3.0eV)



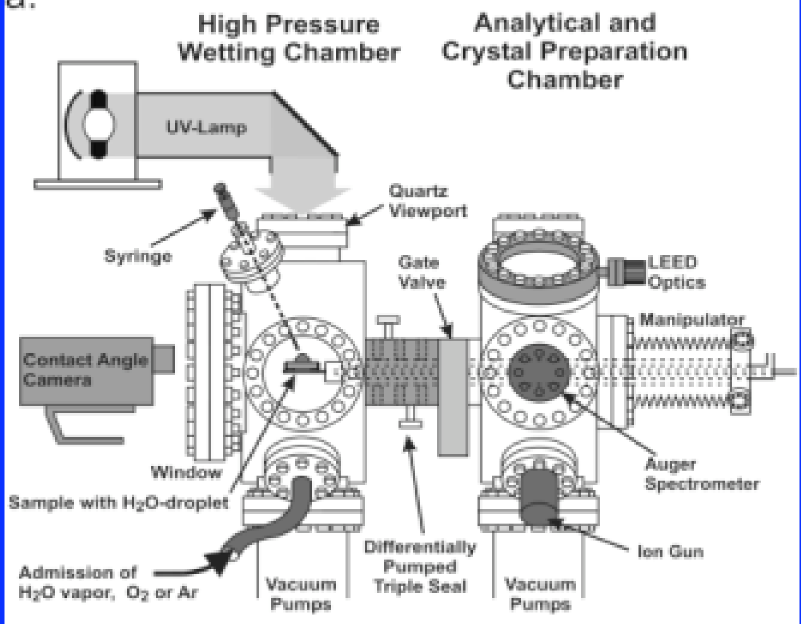
$$Q \leq 10^{-23.5 \pm 0.2}\ cm^2$$

Implies that ~10^8 photons/site do not produce O vacancy defects!

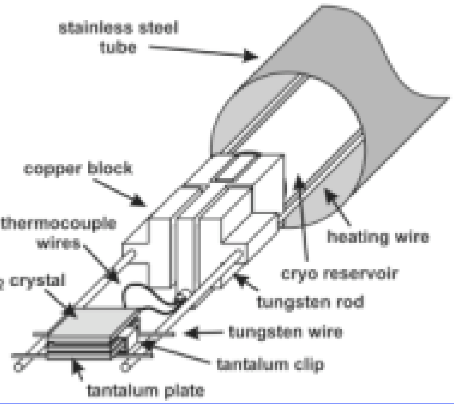
Sergey Mezhenny, Peter Maksymovych, Tracy L. Thompson, Oliver Diwald, Dirk Stahl and Scott D. Walck, Chemical Physics Letters, ***369*** *(2003) 152-158.*

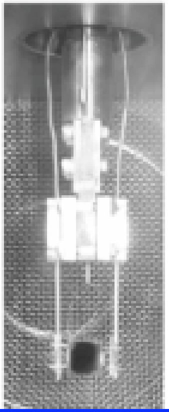
Apparatus for H_2O Contact Angle Measurements on $TiO_2(110)$

a.



b. $TiO_2(110)$ Crystal Mount



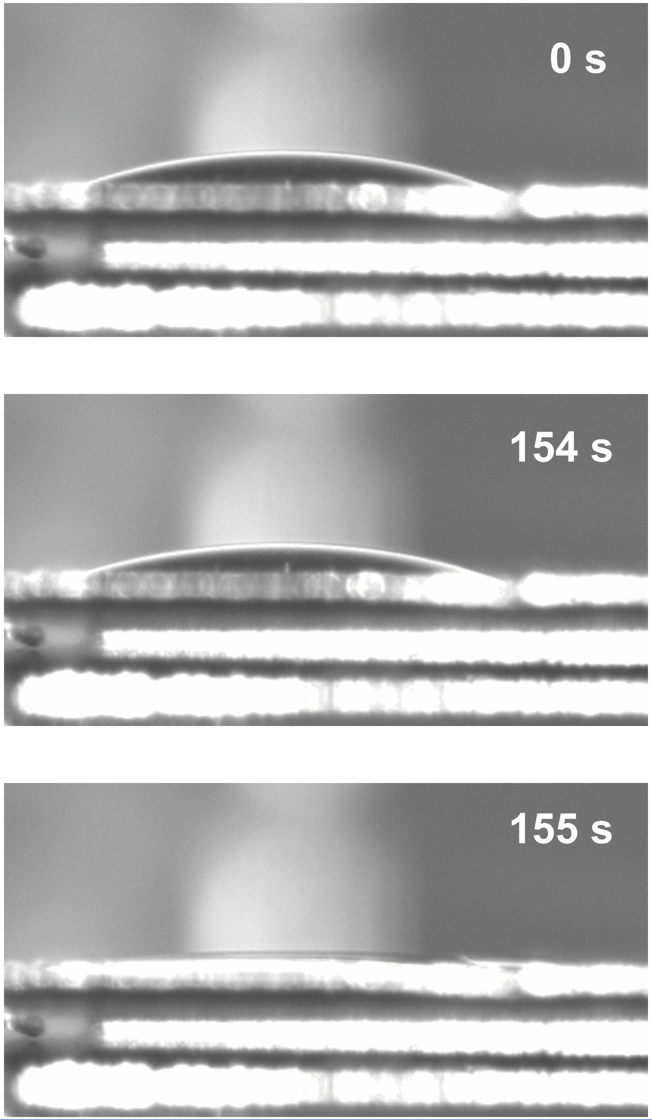


This technology allows study of contact angle for pure H_2O under conditions of:

- well controlled initial surface cleanliness
- well controlled atmosphere
- well controlled photon flux

Typical H_2O Contact Angle Showing Sudden Onset of Wetting of $TiO_2(110)$

P_{O_2} = 1 atm; hexane = 120 ppm

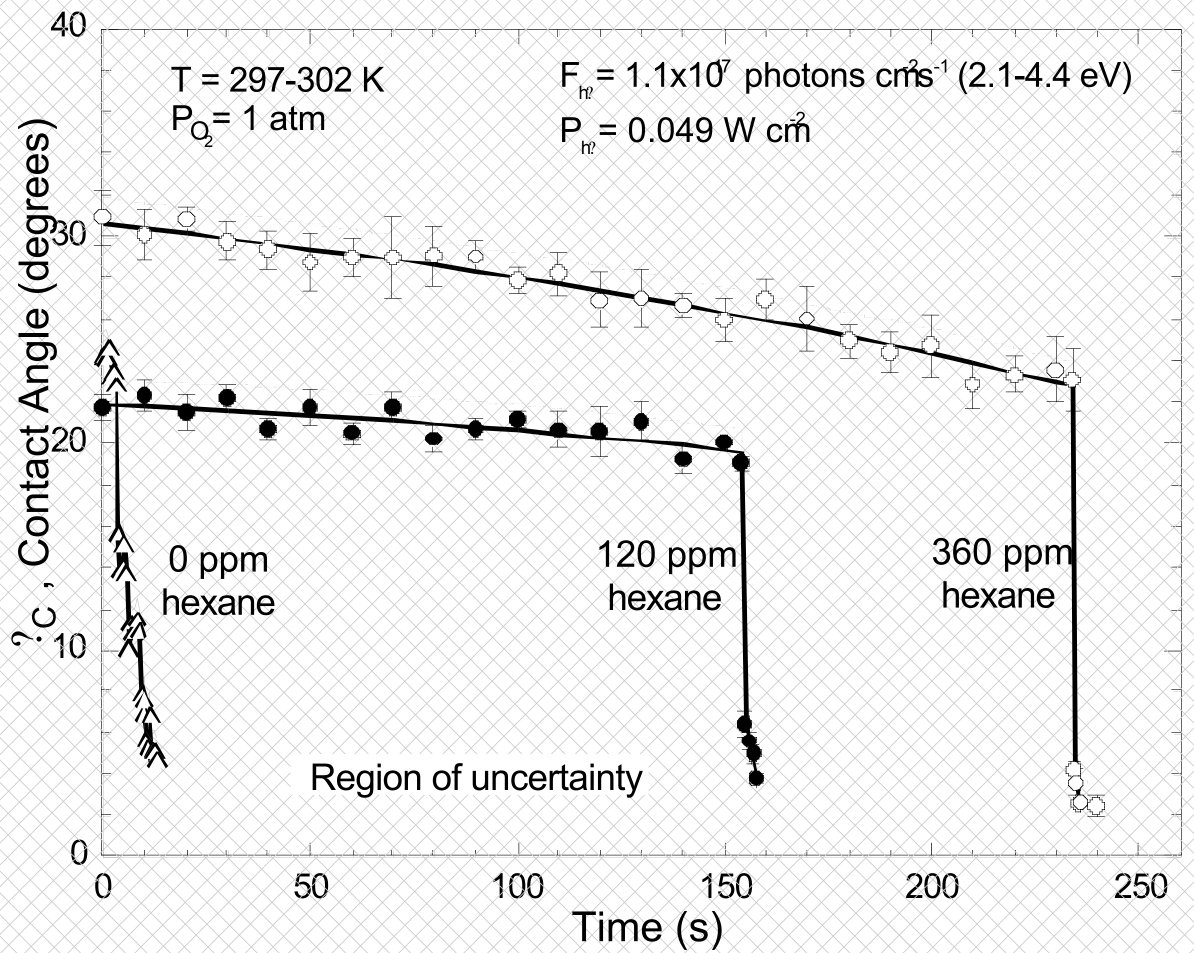


a

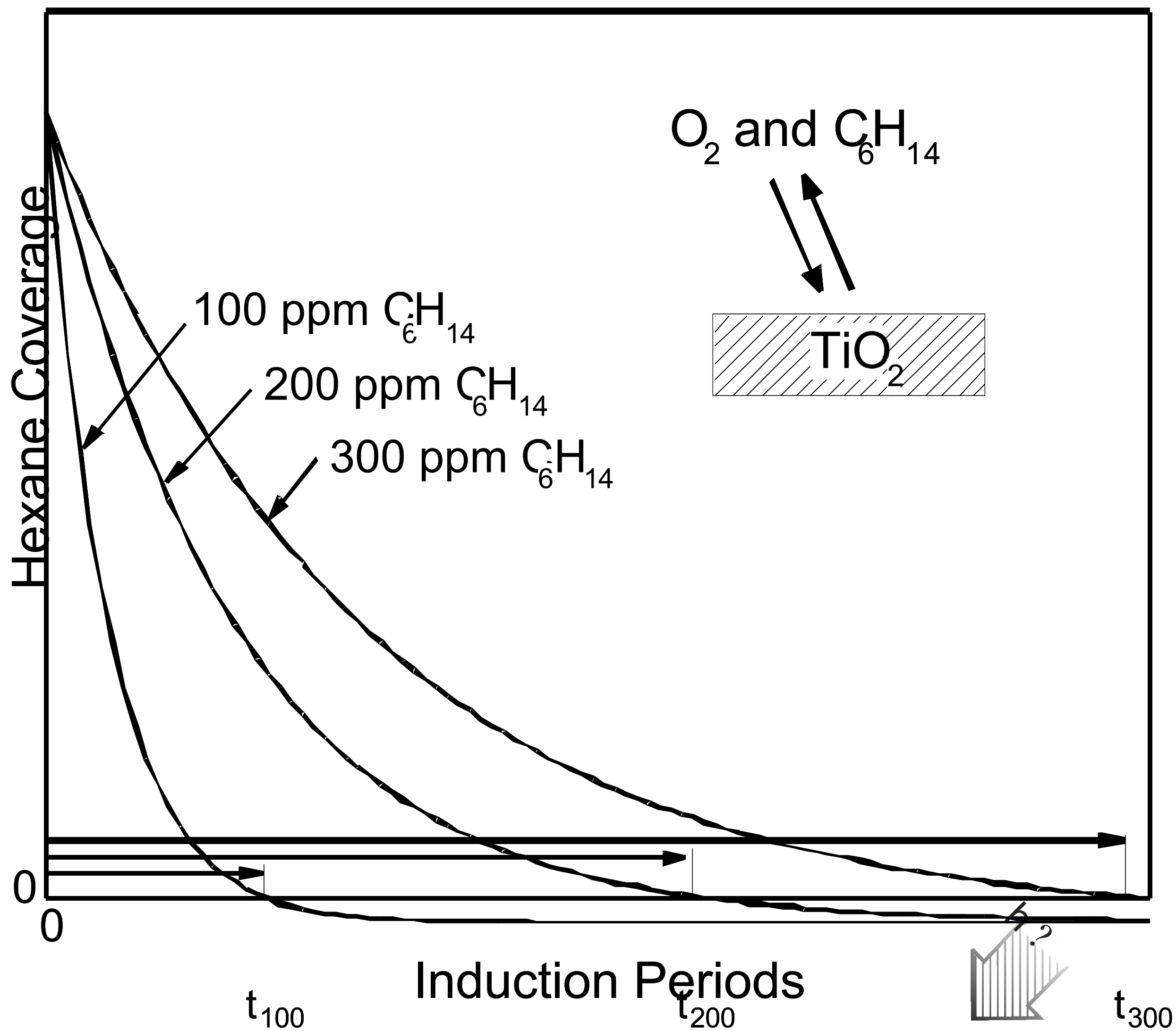
b

c

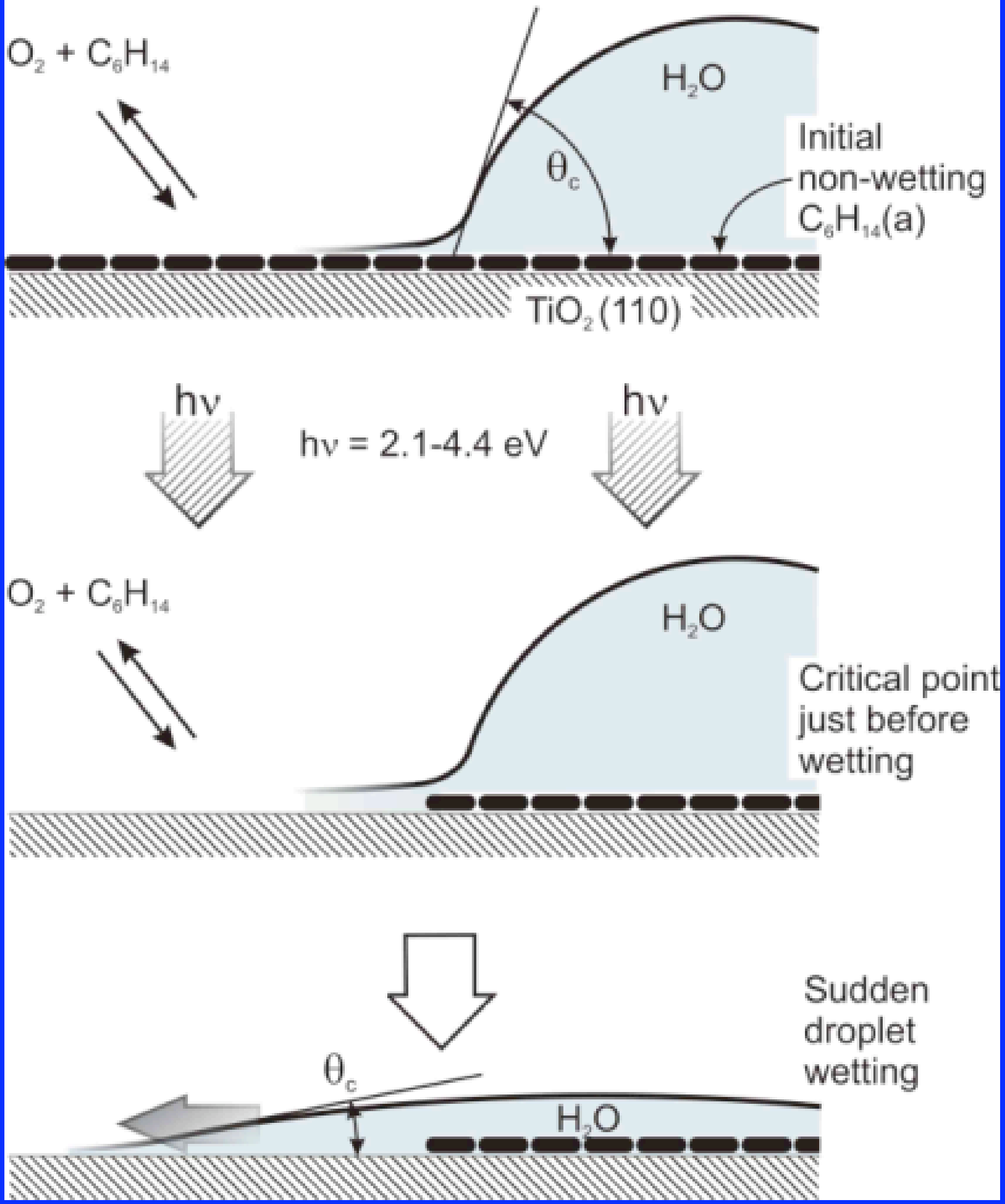
Hexane Vapor Effect on the UV-Induced Wetting of TiO_2(110)



Schematic Origin of Wetting Delay Period



Sudden Hydrophilic Effect due to Hydrocarbon Photooxidation on TiO_2



Conclusions

- Hydrophilicity model involving UV production of O-vacancy defect sites is unlikely based on STM results.

- Hydrophilicity model involving hydrocarbon photooxidation to produce clean wettable TiO_2 is likely to be true.
  - Induction period scales with ppm concentration of hexane in O_2.

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